

HYDROGEOCHEMICAL STUDIES ON
WTC URANIUM TAILINGS LYSIMETERS

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A Report for
CANMET
MINERAL SCIENCES LABORATORIES
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MICROMEDIA

PREFACE

In 1974, Environment Canada initiated a series of tailings lysimeter studies at the Wastewater Technology Centre (WTC) in Burlington, Ontario, to examine the leachability of radio-nuclides and major constituents (TDS, pH) from uranium mill tailings. In addition, the study attempted to assess the effect of two leachate control methods (chemical fixation and vegetation) upon the characteristics of tailings leachate.

Recently, WTC staff have prepared a draft report to present the leaching data from the various lysimeter studies and to interpret the results. In October, 1982, both WTC and CANMET recognized that a unique opportunity existed in this project to assess the chemistry of the tailings and leachate to develop a model for radioisotope mobilization from tailings.

Subsequently, IEC Beak Consultants Ltd. was retained to conduct additional physical/chemical characterization of the tailings solids and some leachate samples. This information, together with the existing data, was then used to develop a conceptual model with which to try to explain the behaviour of the tailings during the leaching of the lysimeters. The specific tasks undertaken included the following:

- o multi-parameter analysis of leachates collected from 4 lysimeters over the last 1 1/2 years of operation
- o physical/chemical characterization of the final lysimeter solids including grain size, bulk density, sulphate and carbonate content.
- o use of Scanning Electron Microscopy (SEM) coupled with X-ray Emission (XRE) spectroscopy, plus Mossbauer spectroscopy to characterize surface precipitates and iron speciation respectively
- o chemical equilibrium modelling on leachates to estimate controlling species in radioisotope and TDS release.

This information was to be incorporated into the final report prepared by the WTC on the uranium tailings lysimeter project. This was to take the form of addition sentences, paragraphs, sections, or appendices as required to complete the interpretation of the WTC data.

The material presented in this report represents only the work performed by IEC Beak, in completion of DSS Contract No. OSQ-82-00216, and has been abstracted from the final WTC report. Consequently this document contains the following information

- o comments relevant to specific pages in the text of the WTC report (eg. 25A represents insert A on page 25 of the WTC report)
- o new sections summarizing the new work and interpretation, numbered to fit with the existing WTC draft report
- o additional appendices describing in detail the work performed
- o new figures and tables for both text and appendices

This information is listed in more detail in the Table of Contents which follows this preface, preceeding the new text.

The findings of the WTC study and the additional work performed by IEC Beak represent a significant step forward in the understanding of the processes and factors in radionuclide mobilization from uranium mill tialings. It is recommended that the reader refer to the WTC report when reviewing the work presented here, so that this work is seen in the context of the overall study.

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SUMMARY

The mining and milling of U-ores removes a mineral assemblage which is stable in a reducing environment, mobilizes some of the reduced minerals by leaching and oxidation, reprecipitates most of the mobilized substances as secondary precipitates upon the host mineral (e.g. as a gypsum in the case of an acid-leach mill) and disposes of them within a tailings management area. In this new environment, oxic conditions may prevail and water flow pathways may be such that percolating waters can pass through the tailings (the name for the solid wastes resulting from mining-milling) and carry mobilized elements to ground and surface waters. In particular, an oxic environment is conducive to the oxidation of reduced sulfide minerals. Because pyrite (FeS_2) dominates these waste tailings, the major elements in leachate from oxic tailings are Fe^{3+} , SO_4^{2-} and H^+ , resulting in a very acidic water. Coincidentally, other heavy metals (e.g. Cu, Ni) which are in sulfide form are also released due to oxidation of their sulfides.

In addition to acidity and heavy metal mobilization, the release of radioisotopes through atmospheric and aquatic pathways are of concern to regulatory authorities concerned with environmental quality (e.g. Environment Canada) and nuclear safety (e.g., Atomic Energy Control Board). Past work has suggested that Ra-226 is the radioisotope of most concern to regulatory authorities due to its radio toxicity. Thorium species are of concern because of their long half life and because Th-230 is the parent of Ra-226. More recent work has suggested that Pb-210 and Po-210 are of equal importance or of more concern to regulatory authorities because they may result in a potentially larger "dose commitment", (a measure of committed damage to the human body), to humans through aquatic pathways than does Ra-226. But because Ra-226 is longer-lived and is the parent of Pb-210 and Po-210, it probably remains the radioisotope of most concern to regulatory authorities examining aquatic pathways.

In response to these concerns, the Wastewater Technology Centre, Canada Centre for Inland Waters, Environment Canada, Burlington, Ontario initiated a series of studies in 1974 to examine the leachability of major constituents (TDS, pH) and radioisotopes from typical U-mill tailings. In addition, the study attempted to assess the effect of two control methods (chemical fixation), and vegetation) upon characteristics of tailings leachate. The original study design was formulated in consultation with the Radioactivity Subgroup of the Federal Mining Task Force whose purpose is to assist the

development of effluent guidelines and regulations for the uranium mining industry and the Environmental Management Service, Environment Canada. Subsequent modifications were made by internal expertise developed during the course of the study and at the suggestion of CANMET personnel. Final characterization of the solids remaining from one experiment (25 year old tailings) was made by IEC Beak Consultants via an external contract initiated by the WTC.

The experiments carried out in the project were four fold.

1. Examine the leachability of old tailings and those containing a large portion of (Ba, Ra) SO_4 sludges.
2. Examine the leachability of (Ba, Ra) SO_4 sludges located at the bottom of settling ponds.
3. Examine the leaching characteristics of new tailings subjected to various treatments (e.g. no treatment, vegetated, chem-fixed).
4. Examine the leaching characteristics of new tailings subject to varying flow rates.

In addition, the microbiology of experiments 2 and 3 was examined.

The actual details of the experiments, their results and analyses are given in the main body of this report. In addition a conceptual model which integrates the results from all experiments is given. The main conclusions derived from this study are summarized here below.

1. During the initial leaching of tailings, dissolution of gypsum and minor amounts of carbonates explain the conductivity, the TDS and the pH of leachate waters. After sufficient dissolution which exposes pyrite grains to biofilm waters containing oxygen, pyrite oxidation becomes possible.
2. Upon the colonization of tailings by pyrite oxidizers the pH rapidly reaches the level of 2-3. Higher values result from the flux of water diluting the mass of (H^+) produced by pyrite oxidation. Continuous modes of water application are hypothesized to slow the rate of colonization compared to a batch mode of application. This hypothesis is used to explain the observation that after

dissolution of gypsum and at the same pore volume, the amount of sulfate and TDS produced is less in continuous-mode lysimeters.

3. In tailings containing no pyrite and upon completion of dissolution of most gypsum from these tailings, the leachate stabilizes at pH 5-6. This is the same pH as the distilled water applied to the tailings.
4. TDS leaching characteristics are controlled by the mass of gypsum available for leaching during initial phases, provided that the solubility of gypsum is maintained. That is, the mass of TDS loss is only function of the rate of water application.
5. During acidic phases, TDS characteristics are independent of the "leachability of pyrite". That is, during pyrite oxidation, the rate of production of TDS is independent of flushing rate (Experiment 1, 4) implying that once bacteria have colonized the tailings, the pyrite oxidation rate is independent of the hydraulic loading (flushing) rate.
6. During acidic phases, the pH can be reasonably predicted given knowledge of the TDS and assuming the chemical electroneutrality condition and that pyrite is the main source of Fe and S. Leachate analysis data from the old tailings suggest that a slight alteration from Fe:S ratio of 0.5 is in order for some tailings - their data suggest a source which is 1/3 FeS and 2/3 FeS₂.
7. Below pH 2.0, the pH of iron sulfate waters does not decrease per unit increase in TDS as fast as it does above pH 2.0 because of complexes formed. For leachate with pH in the range 0.8 - 1.5, Fe(SO₄)₂⁻, FeSO₄⁺, and HSO₄⁻ are the dominant chemical complexes.
8. Measurements of TDS over-estimate the actual TDS of iron sulfate waters by about 30%, and of calcium sulfate waters by about 20%. This error is attributed to the incomplete loss of waters of hydration of the solid formed during evaporation at 105°C. The measurement error for the iron sulfate water correlates well with the value for volatile dissolved solids. For the iron sulfate water, this error probably results from incomplete loss (1/3) of the 6 waters of

hydration which are coordinated as innersphere complexes with Fe^{3+} . For gypsum, they probably represent the 2 waters of hydration of gypsum formed during evaporation; these 2 water molecules are lost at 175°C .

9. Protons formed from pyrite oxidation reactions attack alumino-silicate minerals in the tailings, releasing Al, F, Mg, K, and Si from Nordic tailings. But solubility controls limit the amount of Si that can be released in the leachate, inducing the reprecipitation of Si as amorphous $\text{SiO}_{2(s)}$. Substantial quantities of Al, F and K are also retained in the tailings after proton-attack. Whether they are constituted in secondary alumino-silicates formed from the incongruent dissolution of the parent minerals or are emmeshed in the amorphous $\text{SiO}_{2(s)}$ is unclear.
10. Minor amounts of other heavy metals also flow from the lysimeters. Metals such as Ni and Cu are probably derived from oxidation of their sulfides while others such as Ti probably originate from proton attack upon oxides (e.g., rutile).
11. Thorium species (Th-230, Th-232, Th-228), are precipitated mainly in the final neutralization tank as a $\text{Th}(\text{OH})_{4(s)}$ which is only minimally encapsulated in the gypsum precipitates. When placed in the tailings pile, they are rapidly solubilized when the pH becomes acidic. Because thorium is lost much faster from the tailings than gypsum, it is argued that the initial Th form in the tailings must be as a $\text{Th}(\text{OH})_{4(s)}$ which is essentially separate from that of gypsum.
12. Over the long term, Thorium species observed in leachate from old tailings are derived from proton attack upon residual minerals containing Thorium which was not mobilized in the leaching pachucas of the mill.
13. Ra-226 is retained in disposed tailings, for about 25 years after placement in approximately the same concentration as when the tailings were originally placed. The concentrations in the old tailings of Experiment 1 (120 pCi/gm) are lower than those conventionally associated with coarse tailings (165 pCi/gm) but this difference can be explained by the smaller surface area of these tailings. These tailings are coarser (95% of their masses found in the size class 2 mm to 50 μm) than that conventionally described as coarse tailings (64% between 2 mm and 50 μm).

mm and 50 μ m).

14. Ra-226 has been lost (over 80%) from the top 10 cm of one lysimeter. This release coincides with a decrease in sulfate concentration in the leachate. At this time, pyrite is essentially consumed in the zone from which Ra-226 was released. This suggests that when sulfate production from pyrite oxidation is complete, a sulfate mineral containing Ra-226 and which formed in the leaching pachucas begins to solubilize, releasing Ra-226. Hence these tailings are on the verge of releasing their Ra-226. When the release ceased is unclear. Further work on these lysimeters would rapidly give substantive information on geochemical controls on Ra-226 in tailings over the long term.
15. The loss of Ra-226 upon completion of sulfate dissolution is proven by data from tailings containing no pyrite (Madawaska). Upon complete dissolution of gypsum and when little sulfate is found in the leachate, the loss of Ra-226 increases by an order of magnitude. Such tailings thus provide an excellent source for studying geochemical controls upon Ra-226 evolution without the complication caused by pyrite oxidation.
16. Experiments were conducted, using washing experiments to ascertain which mineral may be maintaining Ra-226 on the surface of the old tailings. Correlations were sought between Ra-226 in the wash water and concentrations of various metals (Pb, Fe, Ba, Ca) using tailings from the leaching pachucas and the middle section of the high rate, old-tailings lysimeter. Barium is the only metal whose concentration gives a consistent correlation with the (Ra-226) activity in the water. The chemical speciation measurements show that only $\text{BaSO}_{4(s)}$ and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) are consistently favoured to precipitate from the leachate waters of low rate lysimeters of the old tailings and $\text{BaSO}_{4(s)}$ from the high rate lysimeter. It is concluded that $\text{BaSO}_{4(s)}$ must be the precipitate controlling the Ra-226 behaviour through the mill and into the tailings pile. Barium can be derived from dissolution of trace quantities of barium minerals in the ore and its subsequent rapid reprecipitation as a precipitate (probably less than 1 μ m in size) on the surface of the host tailings solids in the leaching pachucas.

17. Scanning electron microscope - xray emission (SEM-XRE) analysis was made of solids from the LP, PN and FN of the mill and from the old tailings. The analysis shows that many particles are formed on the host rock particle in the LP and substantially more in the PN and FN tanks. Many of the particles are composed of Al, Si, K, Ca, Fe and S suggesting alumino-silicates, gypsum and pyrite. Several particles have a composition and morphology consistent with ettringite, a mineral formed in concrete reactions. No significant quantities of jarosite or $\text{BaSO}_4(\text{s})$ are identified either by individual examination of particles (1-5 μm in size) or by ultrasonisation to remove the particle from the silicate mineral background. The weathered tailings solids have a substantially lower surface coverage of secondary precipitates than those coarse particles derived fresh from the mill. This is consistent with dissolution of gypsum after placement of these old tailings in the tailings pile.
18. The leaching of Ca, Mg, SO_4 and Ra-226 from $(\text{Ba}, \text{Ra})\text{SO}_4$ sludges in the sediments of lagoons is consistent with dissolution reactions in sediment pore water and the diffusion of these constituents into the overlying water. Leaching from a proprietary encapsulating process applied to these sludges is consistent with the dissolution of (Na, K) (silicate, sulfate) which is not initially well formed. In fact, the subsequent appearance of Ca in the leachate from both a lagoon situation and porous lysimeter situation suggests that the encapsulating material dissolves sufficiently that the CaSO_4 and MgSO_4 character of these sludges also begin to dissolve. That is, the encapsulation process provides neutralization capacity to the tailings but may only delay the development of acidification reactions or the sludges and tailings if pyrite is present.
19. Vegetating tailings with a fescue - red top grass to which a layer of sewage sludge was added as a nutrient and organic matter source, was unsuccessful over the long term. Leachate from the tailings becomes as acidic as quickly as those of controls, and the grasses eventually die.

20. Vegetating encapsulated tailings with a fescue, red top grass to which sewage sludge was added successfully produced a vegetated cover. Furthermore the leachate pH remained neutral during the life time of the experiment (5 years). Whether the vegetation would be successfully maintained over the long term requires further work. Because the experiments are still proceeding, their monitoring in the future would be quite useful. Characterization of their solids in future work would give relevant information for predicting their future state because it is possible that dissolution of the cementating agent, as has occurred in other experiments, would permit the development of pyrite oxidation reactions and the subsequent destruction of the vegetation.

2A

Uranium and other ores are typically associated with reduced minerals in the parent rock. Controversy exists over the exact geological history that resulted in their formation but one can simply describe the overall formation as involving the transport of various metals in a positive oxidation state with hydrothermal or other (e.g. saline waters) fluids to a location where the groundwater had a lower redox potential. At this site, reactions occurred over geological time scales to lower the oxidation state of the metals and induce them to precipitate to form the ore body. The presence of sulfates or arsenates and their reduction to sulfide or arsenides provides for the formation of metal sulfides. Hence the chemistry of milling such ores then involves dissolution of the desired precipitates and their oxidation. The specificity of the dissolving agents produces leaching of some of the reduced minerals and not others (e.g. in the case of pyritic ores it is thought that only small quantities of pyrite are dissolved by proton attack in a hot sulfuric acid solution). Hence environmental dangers from milling processes may be viewed as being threefold; (i) the minerals leached, (ii) the precipitates formed in the mill, and (iii) the leachability of the original ore solids and of the new precipitates in the natural environment.

2B

From the acid leach process (occurring within the leaching pachucas LP), excess acid is neutralized, typically with lime or limestone in the partial neutralization (PN) tanks. This involves pH adjustment from near 0.5 to 2. Addition of calcium induces precipitation of gypsum and other elements from the leach liquor. Little uranium is precipitated during this initial neutralization step.

2C

The leaching behaviour of other U-238 and Th-232 minerals of interest. Mass balance studies suggest that the same portion of Th-230 and Pb-210 as U-238 are leached in the LP (about 90-95%) and enter the acid solution. Ra-226 remains essentially in the solids fraction (Skaeff, 1978). Hence Ra-226 is either not leached, which is improbable, or it is immediately adsorbed or co-precipitated in the leaching pachucas. Available evidence also suggests that 50% of Th-232 minerals (including Th-228) are leached from the parent minerals and enter the leach liquor. These radioisotopes appear to be carried with the leach liquor until the final neutralization tanks where they are precipitated out of solution.

3A

Jarosite is thermodynamically capable of forming in the leaching pachucas (Beak, 1982). Kaiman (1977) suggests that it forms in the mill and is retained in the tailings basin. Its formation and the coprecipitation of Ra-226 with it in the mill is one possible mechanism for retaining Ra-226 on the solids leaving the LP. However, the conceptual model presented in Chapter 9 argues against mill-formed jarosite and for tailings-formed jarosite.

15A

The assessment of similarity is based upon the pH, the TDS and radioisotope concentrations being the same. This means that despite the addition of limestone, pyrite oxidation continued unabated and its acidity was only minimally neutralized. This can be explained by at least 3 alternative explanations. They are: (i) surface coatings formed on the crushed limestone, which prevented dissolution, (ii) limestone dissolution kinetics are quite slow relative to pyrite oxidation kinetics, and (iii) analytical chemistry cannot detect significant differences due to limestone dissolution when leachate pH is low and TDS is high. Relatively slow dissolution kinetics for limestone, under acid conditions is improbable. The TDS of the leachate waters are completely due to iron sulfate (see section 4.4). The masking of the dissolved mass of limestone by iron sulfate is possible for TDS but improbable for pH, if significant amounts dissolve. It is concluded that formation of surface coatings upon the limestone is the most probable explanation for the lack of differences. Possible precipitates which form are described in Section 4.4.

18A

The switch in water application rates may have inhibited the rate of microbial activity responsible for pyrite oxidation (see Chapter 8) by saturating the high-rate lysimeter tailings. Inhibition would occur if the bacteria have inadequate supplies of oxygen, if physical perturbation significantly influence the bacteria, if Fe concentrations in biofilm waters are too low, or if the pH is too high. Physical perturbation is unlikely; the pH appears to be in the optimum range. Data presented later (section 4.5; Appendix A4) show that the pyrite content remaining in both the high and low rate lysimeter solids is approximately the same. Therefore it is argued that the pyrite oxidation rate is relatively unaffected by the change in flushing rate. Hence the change in pH and decrease in TDS between the middle and high rates of water application results mainly from a dilution effect due to the increased flushing rate.

19A

... and 8). The conductivity of the control lysimeter leachate is controlled by its iron sulfate content (see section 4.4, Appendix A.4). There is a linear relationship between conductivity and total dissolved solids on a log-log plot, although laboratory measurements for TDS over-estimate the actual value (Section 4.4). Within reasonable limits, one can calculate the pH; (i) given the waters TDS, (ii) assuming that the molar Fe/S ratio is 1:2 and (iii) invoking electroneutrality. Because the Fe/S molar ratio was less than 1:2 in the control lysimeter leachate, the exact pH calculated will change somewhat. Furthermore as TDS (conductivity) increases, the pH will not linearly decrease because (i) pH is a log scale, (ii) below pH 1.9, a larger percentage of the H^+ complexes with SO_4^{2-} to form HSO_4^- and (iii) an increasing amount of Fe^{3+} and SO_4^{2-} form complexes with lower charge ($FeSO_4^+$, $Fe(SO_4)_2^-$). Overall, an increase in conductivity causes an increase in H^+ concentration and hence a decrease in pH.

19B

The combined pattern of conductivity and pH then can be interpreted as follows. After recolonization of the tailings by T. ferrocanis, a rough equilibrium condition was reached in which a constant production rate of iron sulfate occurred giving a constant pH. When the flushing rate was changed, the TDS and H^+ concentrations of the high rate leachate immediately decreased giving a higher pH. The order of magnitude difference in conductivity can be explained on the basis of an order of magnitude change in flushing rate, assuming that the pyrite oxidation rate remains constant. The constant pattern continued in the low rate lysimeter until 2000 days when the conductivity of the low rate lysimeter shows a dramatic reduction in its value. The cause of this decrease is discussed in section 4.5.1. During the time from 1000-2000 days, the high rate conductivity shows a gradual decrease and the pH a corresponding increase. This suggests that under the condition of continual water application the pyrite oxidation rate was slowly decreasing. Whether this resulted from an insufficient flux of oxygen or a decreasing supply of pyrite is partially assessed in section 4.

21A

The source of the Ra-226 observed in the peak and its probable geochemical control is assessed in sections 4.4 and 4.5. The evidence suggests that all Ra-226 observed in the peak is derived from loss of Ra-226 from the top 10 cm of the control high rate lysimeter solids and that the mass of Ra-226 observed in the peak is only a small fraction of this loss. Hence the remainder of the Ra-226 lost from the surface 10 cm is resorbed (adsorbed, re-coprecipitated) on lower solids. The evidence also suggests that the Ra-226 dissolution is initiated by low concentrations of biofilm sulfates permitting dissolution of $\text{BaSO}_{4(s)}$ precipitates. What is unclear is why the dissolution process ceased. Because these tailings appear to be on the verge of losing their Ra-226, extremely valuable amounts of information about the geochemical controls on Ra-226 could be obtained if the lysimeters were restarted in future work. Restarting will not be a part of this report. But this project has gotten lysimeter solids to the point where some of the original questions of this project could be answered.

22A

Lead-210 in the tailings will be derived from 3 main sites - the residual minerals containing the remainder of U-238, gypsum as a $(Ca, Pb)SO_4$ coprecipitate and as a daughter of Ra-226. For thorium, it is hypothesized that proton attack upon the residual mineral explains its pattern (see Section 4.5). Pb-210 patterns in the leachate do not show the strong decrease over time that Th species do (compare Fig. 14 to Fig. 16). Furthermore, Pb-210 concentrations after 600 days in the high rate lysimeter leachates are much higher than those of Th-230. There is still some sulfate (as gypsum) left in the control lysimeter solids (Section 4.5). Accordingly it is probable that most Pb-210 in the leachate is due to the slow dissolution of residual sulfates. But the dissolution would be minimal at the depth of most active pyrite oxidation because the high sulfate concentration from biofilm waters would suppress dissolution of gypsum. It is probable that dissolution occurs in upper zones and that reprecipitation does not occur - the speciation calculations (Appendix A.2) indicate that neither Pb nor Ca should precipitate given their concentrations in leachate waters. Because Pb-210 masses escaping from the control and $(Ba, Ra)SO_4$ sediment lysimeters are the same, gypsum dissolution in the tailings exclusively control the behaviour of Pb-210 in the sediment lysimeters.

23A

The reader could debate the interpretation given, herein, arguing that all Th observed results from that dissolution of Th formed during the drying of the tailings. During drying, the most probable form of Th is as a $\text{Th}(\text{OH})_4$ or Th enmeshed in a $\text{Fe}(\text{SO}_4)_x(\text{S})$. The low levels of Th found in the solids (see Table A.13B) suggest only Th unleached from residual minerals would remain on the tailings (see Section 4.5). Because there is a correlation between Th concentration and pH, it is concluded that Th patterns result from the capability of protons to attack Th- containing, residual minerals.

25A

At the end of the experiment, leachate samples for the period Jan. 1980 to Dec. 1981 have been analyzed for anions, cations, nutrients and TDS. For several of these leachate samples, measured concentrations have been abstracted to form "model waters" for which chemical speciation calculations were made. These calculations permit statements concerning the probable chemical species present and the probable precipitates which would form. Also, cores from the low and high rate lysimeters have been obtained and various physical, chemical and mineralogical features analyzed.

26A

When the lysimeters were switched from a batch to continuous mode of water application, a near saturated state existed. Bacterial activity would have been limited by the flux of dissolved oxygen with the applied water. Because the quantity of pyrite remaining in the control lysimeter solids is essentially the same in the low and high rate lysimeters, it is concluded that the rate of pyrite oxidation remained essentially unchanged in the high rate lysimeter and that the flux of oxygen did not measurably slow the rate of oxidation.

26B

Chemical analysis of the control lysimeter water and speciation calculations shows that iron and hydrogen sulfate complexes (Fe^{3+} , FeSO_4^+ , $\text{Fe}(\text{SO}_4)_-$, H^+ , HSO_4^- , SO_4^{2-}), dominate the electrochemistry and that the pH can be calculated in a reasonable fashion using values for TDS, an Fe/S ratio based upon pyrite, and electroneutrality. The rate of pyrite oxidation is essentially the same in both high rate and low rate control lysimeters, suggesting that the main effect of flushing is to dilute the mass of iron sulfate produced by pyrite oxidation. Calculations suggest that $\text{Fe}(\text{OH})_{3(s)}$ may have formed on the high rate control while jarosite might have formed in the low-rate control. The amount of such precipitates formed in the control lysimeters is small because the quantity of Fe(III) minerals present is less than 5% of pyrite remaining. The leachate data suggests its iron sulfate content was derived 1/3 from an FeS and 2/3 from FeS_2 during the last 2 years of leaching. The decline in the conductivity of the low rate lysimeter after 2000 days is attributed to insufficient pyrite remaining to allow production of iron sulfate at its former rate. Furthermore, although the conductivity data for the high rate controls do not show it, the concentrations of both TDS, Fe and SO_4 declined by an order of magnitude in both the low rate and high rate controls. This provides further evidence that the pyrite oxidation rate was essentially unaffected by the hydraulic flushing rate.

27A

This geochemical control is concluded to be the maintenance of $\text{BaSO}_{4(s)}$ solubility limits until elimination of sufficient pyrite such that sulfate concentrations in biofilm waters declined and allowed dissolution of the $\text{BaSO}_{4(s)}$ solid containing Ra-226. This argument is new for old tailings. The formation of a (Ba, Ra) SO_4 precipitate on the quartz particles in the leaching pachucas in the mill is supported by experimental evidence presented herein; the maintenance of such a solid in the control lysimeters (old tailings) is supported by chemical speciation calculations.

27B

The patterns of release of Pb-210 from the control lysimeters are hypothesized to be due to dissolution of residual gypsum minerals and their associated content of Pb-210. This is based largely on an argument that Pb-210 is carried through the mill in solution until it is brought down by gypsum precipitation in the final neutralization tank. The patterns of thorium release are consistent with a mechanism involving proton attack upon residual minerals containing thorium - at lower pH's proton attack liberates more thorium. The low thorium content of the lysimeter solids is consistent with that expected after acid leaching of the ore in the leaching pachucas. But both Pb-210 and thorium should be mobilized equally in the leaching pachucas. Hence it might be expected that an equal quantity of thorium and lead could be found in the gypsum formed in the final neutralization chambers. Because thorium readily forms $\text{Th(OH)}_{4(s)}$ and has few sulfate complexes, while lead has a larger fraction in sulfate complexes at pH 8, it is probable that thorium exists mostly as a $\text{Th(OH)}_{4(s)}$ while lead is coprecipitated as (Ca, Pb) SO_4 in the gypsum solid. Hence dissolution of some of the gypsum and complete removal of $\text{Th(OH)}_{4(s)}$ by proton attack during the first years after tailings disposal provides for a significant residual quantity of mill-mobilized Pb-210 and not of thorium species.

28A

The chemical analyses of the leachate show that in addition to iron sulfate, high concentrations of Al, K, Mg, Ca, F, and Si are present as well as smaller concentrations of Cu, Co, Ti and Ni. The Al, K, Mg, F and Si concentrations are attributed to the dissolution of primary alumino-silicates by proton attack; SEM-XRE analyses suggests that plate shaped particles of size $2\text{ }\mu\text{m} \times 10 \times 10\text{ }\mu\text{m}$ are likely candidates for the elements. In addition, it is possible, although not likely, that some of the host quartz solids whose size dominate the particle size distribution measurements (i.e. $50\text{ }\mu\text{m} - 2\text{mm}$) are also undergoing proton attack. The concentration of these elements increases with increasing H^+ (i.e. decreasing pH) indicating that proton attack on the alumino-silicate matrix is the most probable mechanism for their liberation. But analyses of various metal ratios in the control lysimeter leachate suggest that some of the K, Al and F liberated during proton attack is reprecipitated in the tailings solids. The analyses also suggests that over 90% of Si liberated by proton attack is retained by formation of amorphous $\text{SiO}_{2(s)}$. The formation of amorphous $\text{SiO}_{2(s)}$ is justified by the maintenance of a constant concentration of (Si) in the leachate whose value is that of the solubility product of $\text{SiO}_{2(s)}$. Whether the other elements (Al, K, F) are retained due to the formation of new alumino-silicate by incongruent dissolution of parent alumino-silicates or whether they are coprecipitated with amorphous $\text{SiO}_{2(s)}$ remains unanswered, although SEM-XRE spectroscopy of amorphous silica particles show the presence of Al, K and Fe.

The sources of Cu and Ti are hypothesized to be small quantities of sulfides (e.g. chalcopyrite, CuFeS_2 for Cu) while Ti may originate from rutile.

Minor quantities of Ba, Cd, Mn, Pb, V, Zn, and Cl were also measured in the leachate waters. The Ba concentrations are typically at levels consistent with formation of $\text{BaSO}_{4(s)}$. Because the analytical methods used do not determine Ba as accurately as Mn, for example, it would be useful to measure its concentration more accurately in future work, to ascertain more accurately whether it is at equilibrium with $\text{BaSO}_{4(s)}$ throughout the time period of the decrease in TDS in the control lysimeters. The other minor elements are assumed to result from proton attack upon trace quantities of minerals containing them which exist in the tailings.

Particle size distribution measurements on the control lysimeters show that 95% of the

tailings lie between 2mm and 64 μm . Their porosity is 0.58. This means that they are quite coarse tailings. Their Ra-226 content (120 pCi/g) is smaller than that previously observed for coarse tailings (160 pCi/g), but the difference can be explained by the smaller surface area of coarse tailings.

Mineralogical and physical analyses indicate that surface precipitates (1-10 μm) are formed on the coarse quartz particles in the leaching pachucas. These particles are probable sites for the co-precipitation of Ra-226. A denser coverage is observed in solids from the neutralization tanks. Particles whose composition and morphology are consistent with those observed in cementation reactions (a calcium sulfate aluminate hydrate) are observed in addition to gypsum type particles. Most of the particles have been wash off the lysimeter solids. This probably results from the early dissolution of calcium sulfate solids after tailings disposal.

28B

Evidence gathered suggests that Ra-226 will be maintained in a solid form until biofilm concentrations of sulfate decrease to permit dissolution of the $(\text{Ba,Ra})\text{SO}_4$ coprecipitate. This is true even for tailings without the $(\text{Ba,Ra})\text{SO}_4$ sludges. Hence, the Ra-226 release will ultimately be proportional to the initial content, but its time history will depened upon the amount of pyrite initially present and its time history of oxidation. A similar argument can be made for Th contained in the $(\text{Ba, Ra})\text{SO}_4$ sludge. On the other hand, the time history of thorium evolution from residual minerals will be a function of biofilm acidity and the length of time that it is maintained.

35A

The chemical data (Table 10) provide some explanation for the observed pH and conductivity trends. The lack of alkalinity measurements preclude complete statements about controls on pH. The water from the controls is essentially a calcium, magnesium sulfate while that of the Chem Fixed sediments is a sodium, potassium silicate sulfate with minor amounts of aluminum. The concentration of both waters decreases over the 5 year period from 1976 to 1980. Accordingly, it is probable that the constituents of both waters result from the diffusion of pore water elements into the pond water and their subsequent outflow. The gradual decrease of conductivity in the controls suggest that the (Ba, Ra)SO₄ sludge is essentially at equilibrium with its pore water, while the peak in the treated sediments suggest that they are not at equilibrium with their pore waters. A two year period for dissolved constituents to diffuse from 13-16 cm of sediments is not unrealistic, although crystallization dissolution reactions from the solid phase may have also supplied material to the sediment pore water. The slow decrease in conductivity during the last 2 years suggests that dissolution reactions were continuous but that dissolution and diffusion from the sediments was somewhat slower than hydraulic washout.

The exact composition of the sediments is not clear from the leachate data. Application of a lime BaCl₂ treatment to the overflow water from the tailings pond containing much sulfate means that extensive quantities of CaSO_{4(s)} and BaSO_{4(s)} are formed. But if significant quantities of Ba(SO₄)_(s) did dissolve, it is expected that significantly higher concentrations of Ra-226 would be observed in the overflow water. Hence, it is probable that only small quantities of the (Ba, Ra) SO₄ sediments are dissolving; measurements of Ba are not available to confirm this point. With this assumption, one can conclude that the sediment pore water is essentially governed by dissolution of (Ca, Mg) sulfate and minor amounts of CaCO₃. Measurements of carbonate are required to explain the pH of 8.0.

The composition of the leachate water from the Chem Fix sediments is again assumed to be governed by dissolution of the solids dominating the CF sediments. The data suggest that the solid is mainly a (Na, K) (silicate, sulfate). Because Ra-226 concentrations still occur at one-half the levels of the controls and because the calcium concentration increases over time, it is probable that the Chem Fix process incompletely encapsulates the (Ba, Ra) SO₄ sludges enmeshed in CaSO₄, or that dissolution of the Chem Fix solid allow some dissolution of the (Ba, Ra) SO₄ sludge.

53A

This occurs despite the higher flushing rate which would more quickly have exposed pyrite grains to oxygen.

53B

The higher flushing rate does have an effect upon leaching - it slows down the rate of colonization of tailings by T. ferrocanis but not the rate of oxidation once the bacteria are colonized.

56A

From certain perspectives, these observations are at variance with the data presented for experiment 1 (sections 4.5.3 and A.4) which suggest that Ra-226 leaching patterns are controlled by $\text{BaSO}_{4(s)}$ solubility considerations. That is at higher sulfate concentrations (lower pH's) less Ra-226 should dissolve because less $\text{BaSO}_{4(s)}$ can dissolve whereas this experiment suggests Ra-226 increases as the pH decreases. But the actual variation with pH appears to be small compared to the variation of Ra-226 leached as a function of leachate volume. In the mill, some Ra-226 is carried with the leach waters until it is finally precipitated with gypsum in both the partial neutralization and final neutralization tanks. Continual dissolution of small amounts of gypsum and its coprecipitated Ra-226 over long time scales is probable. Residual gypsum still exists in the old tailings of experiment 1, 25 years after their abandonment. Larger leachate volumes provide for dissolution of larger masses of gypsum by maintaining lower concentrations of sulfate in the leachate water and increasing the dissolution kinetics of gypsum. This assumes that the residual gypsum has slower dissolution kinetics than that which dissolves during the first several pore volumes when the conductivity is maintained at a high value.

57A

This trend is consistent with gypsum dissolution maintaining sulfate concentrations during the first 10 pore volumes. After this, the readily dissolvable portion of gypsum (that formed in the final neutralization tanks) has been removed allowing a drop in pore water sulfate concentrations. At the same time, pyrite oxidizing bacteria have commenced to colonize the tailings. This results in increased sulfide oxidation and an increase in sulfate concentration after 12-13 pore volumes.

57B

These observations are consistent with the arguments advanced above concerning the time of colonization of pyrite-oxidizing bacteria in lysimeters which have a continuous mode of water application. They suggest that the time of colonization is also influenced by the hydraulic flow rate because more sulfate is produced in low rate lysimeters than higher rate lysimeters at the same pore volume.

60A

These patterns are interpreted to mean that readily dissolvable gypsum formed in the FN, is dissolved during the first period and that a gypsum which is harder to dissolve (e.g. FN and PN formed gypsum) control during the second period. Because the pH never fell below 5-6, and because little pyrite exists in these tailings, no sulfate from pyrite oxidation exists in this leachate. Hence the conductivity is completely dominated by dissolution of gypsum. The low conductivities of 0.1 mmho/cm are due to dissolution of residual gypsum (e.g. as still exists in the old tailings of Experiment 1) and other ions.

4.4 Chemical Analyses of Leachate from Experiment 1

Leachate samples from the last 1.5 years of the old tailings were analyzed for major cations, major anions, and various trace metals. There were 4-6 samples per lysimeter available for chemical analysis. The samples cover the period from December 1979 to August 1981. The lysimeters ceased operation in late 1981. This period is particularly useful because it covers a decline in TDS and an increase in pH. For the low rate lysimeters, the TDS decreased from about 280 g/L to about 30 g/L while the pH increased from 0.7 to 1.5. For the high rate lysimeter, the TDS declined from about 1.5 g/L to about 0.1 g/L while the pH increased from 2.3 to 3.1. Both chemical changes represent an order of magnitude change in the concentration of aqueous chemical species in the leaching water. Hence it provides powerful evidence for suggesting that major biogeochemical changes have occurred during this period because the previous period of the tailings (i.e. previous 2-3 years) had fairly constant chemistry.

The dates of sampling the leachate (i.e. samples from the period of Dec. 1979 - Aug. 1981), the TDS and pH of the samples at the time of collection, and the concentrations of anions and cations measured in these leachate samples are given in Appendix A in Tables A.1(a) and A.1(b). These measurements show that the concentrations of iron and sulfate are the highest of all cations and anions. That is, one can simply describe the TDS as being approximately equal to iron plus sulfate concentrations. Two questions then arise: (i) how much error is associated with this approximation for TDS and (ii) can the pH be explained by using the measured concentrations of iron and sulfate.

Other questions of interest relevant to the management of water quality and uranium tailings also arise. They include:

- (i) In such a high sulfate water, what portion of each metal is in a free state and what portion is complexed with sulfate and other anions?
- (ii) Do any of the metals have sufficiently high concentrations that they are close to precipitating as a solid?
- (iii) What bacterial yield of nitrogen and carbon is found in these lysimeters?

To examine these and other questions, and indepth analysis and technical discussion of several aspects of the chemical constituents of the leachate samples are given in

appendix A. In A.1, the degree of charge balance attained in the measurements and a comparison of measured and calculated TDS concentrations are described in the section entitled "cationic-anionic balances". In A.2, the probable speciation of most cations and anions are given in a section entitled "cation-anion speciation". The speciation estimates are made by selecting 10 of the leachate samples and using equilibrium chemistry constants to calculate speciation. For example, for iron and sulfate, the calculations provide estimates of the concentration of H^+ , HSO_4^- , SO_4^{2-} , Fe^{3+} , $FeSO_4^+$, and $Fe(SO_4)_2^-$. In A.2, the possible formation of various solids such as $BaSO_4(s)$, $CaSO_4(s)$, amorphous $SiO_2(s)$ and secondary aluminosilicates are also examined using both the speciation calculations and ratios of various metals (e.g. K/Al, F/Al, Ca/Al, Mg/Al, Si/Al and K/mg). Metal ratios are used because, under the assumption that the metal used as the normalizing quantity (the denominator) is conservative, deviation of the ratios in the leachate from that of the lysimeter solids infers that the metal in the numerator is being dissolved but partially retained in the solids. In Appendix A.3, the biochemical characteristics of the leachate are examined using ammonia or carbon produced per mole of iron or sulfate oxidized.

For this section of the report, a summary of the major findings of the appendix is now presented. For the reader interested in the more detailed analysis, the relevant Appendix section should be referred to. A few tables and graphs are extracted from Appendix A and repeated here in the main text. This allows the reader to view the information without need to refer to the appendix.

In particular, for the speciation calculations, Bejurrum diagrams ($-\log C$ vs pH) are constructed for one model water sample from the low rate lysimeter and one model sample water from the high rate lysimeter and given in the appendix. A Bejurrum diagram is a plot of the concentration of various species and complexes versus pH. Diagrams are presented for Al, Ba, Fe, Ca, Th, Ra and SO_4 . The dominant forms of these and other metals are also given in the Appendix. The terminology, "model water" is used instead of leachate water to emphasize the following points: (i) that the specification of all chemical constituents of the leachate water is incomplete, (ii) that the thermodynamic data which describe the complexation and precipitation - dissolution reactions may have errors associated with them and (iii) that the number of complexes known to form, given present day knowledge, may actually be incomplete.

The major findings of the analysis presented in the appendix are the following.

1. The major anions and cations in the leachate from the old tailings are iron, sulfate and their complexes. Assuming that the oxidation state of these ions is as Fe^{3+} and SO_4^{2-} , iron chemistry is calculated to be dominated by sulfate complexes ($\text{Fe}(\text{SO}_4)^+$, $\text{Fe}(\text{SO}_4)_2^-$) in leachate from the low rate lysimeter and by hydroxo complexes and $\text{Fe}(\text{OH})_3(s)$ in the high rate lysimeters. Because the iron leaves the lysimeter in a soluble form, its kinetic character must be sufficiently slow to prevent the precipitation of aqueous iron, because the calculations suggest that $\text{Fe}(\text{OH})_3(s)$ may be forming in the tailings solids. Sulfate chemistry is dominated by iron sulfate complexes in the high-rate lysimeter leachate and by its free form (SO_4^{2-}) in the low rate lysimeter. Minor amounts of HSO_4^- are calculated to occur in all leachates.

The shift in dominant species between the low rate and the high rate lysimeter leachate occurs because the higher pH in the high rate leachate provides more hydroxyl ions for complexing iron and because the sulfate concentration is lower. In most leachate waters with pH- 2, HSO_4^- would be the dominant complex if iron were not present. HSO_4^- is not the dominant complex because the iron is able to compete better for SO_4^{2-} than does H^+ .

2. The sum of anions and cations by weight (i.e. the calculated TDS) is consistently less than measured TDS by approximately 30%. Possible causes of this inconsistency include unknown ions not measured or volatilization of ions such as sulfate. Both are improbable. It is hypothesized that the difference occurs due to retention of waters of hydration associated with iron. When the TDS test is carried out, a sample is evaporated at 105°C . Iron has 6 water molecules coordinated as inner sphere complexes. The retention of approximately two water molecules in association with an iron sulfate salt formed during evaporation can explain the difference between calculated and measured TDS.

Measurements for volatile dissolved solids (VDS) have been made on the TDS samples. When VDS is added to the sum of anions and cations, this quantity approximately equals measured TDS. VDS normally is a measure of organic carbon and carbonate solids formed during evaporation. But the leachate has essentially no

carbonate present; TOC is less than 1% of TDS. VDS can be explained as being the loss of waters of hydration from the iron sulfate salt formed during the TDS measurement.

Similar arguments are made for waters dominated by calcium sulfate (see Section 7) in which the measured TDS is about 20% larger than can be explained by the solubility product of gypsum. Two waters of hydration in gypsum can explain this difference.

The differences between calculated and measured TDS mean that estimates for dissolved solids loss from the old tailings lysimeter over its leaching history must be decreased by about 30%.

3. The mineral acidity (titration with base to pH 4.5) of the leachate agrees reasonably well with measurements of sulfate and nitrate concentrations of the water. The electroneutrality of these waters appears to be explainable by Fe^{3+} and SO_4^{2-} concentrations, provided that the complexation of SO_4^{2-} with H^+ , particularly at pH's less than 2, is properly accounted for. This suggests that it is reasonable to assume that both iron and sulfur in leachate water, leaving the lysimeter are fully oxidized. Because the leachate samples were stored for 1-2.5 years before analysis for concentration of ions, this cannot be thoroughly proven. The occurrence of coloured compounds and the remains of bacteria (presumed to be T. ferrocanis) in samples from the low rate lysimeter suggest that some of the iron in such samples leaves the lysimeter with a 2+ oxidation state (i.e. as Fe^{2+}).
4. A linear relationship is observed between the log of TDS and log of conductivity in leachate from these lysimeters; if HNO_3 has been added, the data points lie off this line. It is concluded that conductivity can be used as a surrogate parameter to estimate TDS provided that the water is dominated by one major cation and one major anion (e.g. an iron-sulfate water, or a gypsum water).
5. The iron/sulfur molar ratio varies from 0.5 to 0.75 (average 0.677 ± 0.069) in leachate from the low rate lysimeter and from 0.1-0.65 (average 0.344 ± 0.198) in the high rate lysimeter. Theoretically, the ratio should be 0.5 for pyrite (FeS_2). If the value is larger than 0.5, one could argue that sulfate oxidation is incomplete but this is

rejected. It is possible that the iron sulfide which is oxidized consists of two different sulfides. A source consisting of 1/3 of FeS (e.g. mackinawite) and 2/3 FeS₂ (e.g. pyrite) explains this ratio. The existence of FeS is probable because iron found in the leaching pachacus most probably results from leaching of FeS in acid solution - pyrite is relatively unaffected by H₂SO₄.

Values of Fe/S of less than 0.5 can be explained by iron precipitation in the lysimeters as Fe(OH)_{3(s)}. Such ratios are found mainly in leachate from the high rate lysimeter. This is consistent with the speciation calculation (section A.2) which predicts iron hydroxide should form readily in many of the leachates from the high rate lysimeter

6. Examination of the ratios of F/Al, K/Al, Mg/Al, Ca/Al, Si/Al and K/Mg (see Section A.2) suggest that F, K, Al and Si are being dissolved by proton attack upon the parent lysimeter solids but are also being partially retained in the lysimeters. It is suggested that secondary alumino-silicates and amorphous SiO_{2(s)} are the probable precipitates being formed, although formation of amorphous SiO_{2(s)} which entraps F, K and Al would also be a probable explanation.

There are two pieces of evidence for amorphous SiO_{2(s)} formation. Firstly the concentration of Si in the leachate waters appears to have been constant throughout its leaching history until the switch in pH occurred in the high rate lysimeters; this concentration is that expected if the leachate water is at equilibrium with amorphous SiO_{2(s)}. Secondly, particles which are mainly Si and whose morphology is consistent with that of amorphous SiO_{2(s)} have been identified by SEM-XRE techniques.

Formation of these precipitates also provides a mechanism for co-precipitation of other metals (e.g. Ra-226) if they are liberated in the leachate. The Ra-226 shows a peak in high-rate lysimeter leachates during the last 2 years of its leaching history. Alternative explanations for it commencing and then stopping are given in A.4. It is improbable that formation of amorphous SiO_{2(s)} would have a pronounced effect upon the peaking behaviour of Ra-226 because formation of SiO_{2(s)} is expected to have been a continuous process throughout the lifetime of the lysimeter. If co-precipitation is occurring, it is expected to be a continuous process.

7. The speciation calculations suggest that five other solids could occur readily if iron and sulfate concentrations are higher or if the pH is lower than found in the lysimeter leachates. Four of the solids are $\text{Fe}(\text{OH})_{3(s)}$, $\text{TiO}(\text{OH})_{2(s)}$, $\text{BaSO}_{4(s)}$ and $\text{Co}(\text{OH})_{3(s)}$. The hydroxo solids are pH dependent while the barium solid is sulfate dependent. A fifth solid, an iron sulfate solid, is not evaluated in the speciation calculations but its saturation index suggests that jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) could form in the low rate lysimeter. Analysis of the stability field (see Brown, 1971) suggests that jarosite would form particularly well in the low rate lysimeter while $\text{Fe}(\text{OH})_{3(s)}$ would form particularly well in the high rate lysimeter.

The higher iron and sulfate concentrations described above would occur in the lysimeter biofilms while the higher pH could occur in the upper layers of the lysimeters. The SEM-XRE analyses (see section 4.5.2) did not find any significant mass of these solids although several samples showed locally high iron and sulphur levels with no evidence of pyrite crystal morphology. For iron, the lack of clear identification of the hydroxide or of jarosite in some samples results from the presence of pyrite preventing the clear identification of other iron solids. But the colour, particularly of the high rate lysimeter solids is consistent with the presence of iron hydroxide and/or iron sulfate solids (bands of reddish-brown and yellow-orange colours - see Appendix A.4).

Of particular importance to understanding the Ra-226 leaching patterns is the stability field of $\text{BaSO}_{4(s)}$. Figure 4.4.1 shows the proportion of barium in solid form as the pH is varied from 0 to 3. The sulfate and other elemental concentrations approximate those of the low rate lysimeter leachate in January 1980 before the TDS decreased - the actual pH of the leachate water was 0.7. The diagram suggests that a small quantity of $\text{Ba}(\text{SO}_4)_2$ might precipitate at pH 0.7. That is, the leachate water is approximately at equilibrium with $\text{BaSO}_{4(s)}$ and hence $\text{BaSO}_{4(s)}$ dissolution would be minimal. Because the Ba concentration measurements have an error of greater than 20% associated with them due to the method of analysis, stronger statements about the formation of $\text{BaSO}_{4(s)}$ can not be made. But these data (and also other data presented in Appendix A.4) suggest that Ba in the leachate is at equilibrium with $\text{BaSO}_{4(s)}$ throughout the lysimeter leaching history. Three other solids are typically suggested as possibilities for co-precipitating Ra-226 and

maintaining it on the solids of the leaching pachucas. They are PbSO_4 , CaSO_4 and jarosite. Neither of the first two are predicted to form in the lysimeter leachate. Jarosite could form, particularly in the low rate lysimeters. This suggests that jarosite and/or $\text{BaSO}_4(\text{s})$ are only the two probable solids that could form in the mill, maintain, and control the Ra-226 leaching pattern observed near the end of the leaching history of the high rate lysimeter. Jarosite is not favoured to form in the high rate leachate (Sec. A.4); rather iron hydroxide is favoured to form. But because jarosite could form in the mill, its dissolution in the form of a pulse on associated release of Ra-226 and the reprecipitation of $\text{Fe}(\text{OH})_3(\text{s})$ which does not entrap much Ra-226 could explain the observed Ra-226 peak.

Conclusions concerning the probable mineral which controls Ra-226 leaching behaviour e.g. jarosite or $\text{BaSO}_4(\text{s})$ during lysimeter leaching are presented in Section 4.5.2.

8. The biochemical yield from the high rate lysimeter is 170 mMC/M Fe. This compares favourably with other pyrite oxidation studies. That of the low rate lysimeter is about 10% of this value. The yield from the two lysimeters should be the same. It is suggested that the value for the low rate lysimeter is a net yield, resulting from the decay of pyrite-oxidizing organic matter by other heterotrophes.

A similar difference in yields is observed for nitrogen. It is improbable that the nitrogen is lost by decay because nitrifiers are inactive at low pH. Calculations are presented which show that loss of ammonia by volatilization (at pH 1) is the probable mechanism (see A.4), despite the concentration of NH_3 being approximately 8 orders of magnitude lower than that of total $\text{NH}_3\text{-N}$ (i.e. $\text{NH}_3 + \text{NH}_4^+$).

4.5 Characterization of Lysimeter Solids

Cores were obtained from each of the lysimeters (L1, L2, L7, L8) and analyzed for chemical (sulfide, sulfate, and carbonate) composition, and physical parameters (porosity, moisture content and bulk density). Some measurements of Ra-226, Th-230, Th-232 and Th-228 remaining in the solids have been completed to date. These data plus a physical description of the cores are given in Appendix A.4. Mineralogical features of certain lysimeter sections have been made using Mossbauer and Scanning-Electron - Microscope, X-ray Emission (SEM-XRE) techniques. These data are described in Appendix B.

4.5.1 Physical and Chemical Characteristics

A detailed assessment of the chemical and physical characteristics of the lysimeter solids upon termination of the leaching is given in the Appendix A.4. This assessment permits the following statements concerning the lysimeter leaching patterns.

1. The measured porosity is 0.52; correction for compaction during coring gives a value of 0.58. This means that the number of pore volumes on the graphs (leachate concentration versus pore volume) is high by about 30%.
2. Moisture is still found in the solids, 1 year after cessation of operation. This provides for the maintenance, time to present, of a viable but sessile community of pyrite oxidizers. The higher moisture content at the bottom of the lysimeters suggests that water constituted a minimum of 0.2% of the lysimeter volume during its operation.
3. There are no carbonates present (detection limit, $\sim 0.001\%$), but some sulfate (expressed as gypsum equivalents) remains. In the mill, gypsum will form in the partial neutralization (PN) tanks while both gypsum and carbonates should be added to the solids in the final neutralization (FN) tank. It is probable that the carbonate dissolved many years before these lysimeter solids were retrieved for the leaching studies.

It is concluded that leaching patterns were unaffected by carbonate dissolution at any time during lysimeter operation and that some or all of the calcium observed in

the leachate results from slow dissolution of the residual sulfates. The slow dissolution will result partly from coatings (e.g., secondary minerals formed in the tailings) and partly from the high sulfate concentrations of biofilm water. Because the saturation index for gypsum in leachate waters is much less than 1, slow dissolution kinetics are suggested. But the effect of sulfate concentration cannot be ruled out because the sulfate concentration of biofilm waters may be 1 to 2 orders of magnitude higher - only at the biofilm scale can actual solubility controls be irrefutably evaluated.

4. Some pyrite remains at all depths of the lysimeter; most of it has been oxidized throughout the top three-quarters of both the low and high-rate lysimeters. Assuming that more oxidation has occurred in the high rate lysimeter, less pyrite is expected to remain in the high than low rate lysimeter. This pattern is observed for two lysimeters (L1, L8) but it is inconsistent for two others (L1 and L2). Surface coatings on pyrite particles of one high rate lysimeter (L2) may explain part of these results. But overall it appears that the mass of pyrite remaining is essentially the same in both low and high rate lysimeters.

SEM-XRE and visual characterization show that the pyrite occurs as single cubes (of the order of 1-2 μm long per side), or as in clusters attached to the host solids, and in lenses visible to the eye in the lysimeter solids. Hence when the solids were homogenized before insertion into the lysimeters, the layering and lens character of the tailings pile was not completely eliminated.

The generally low levels of pyrite explain the drop in TDS in the lysimeter leachate. That is, the pyrite composition had reached a sufficiently low level by 1980 that there was insufficient pyrite available to maintain the iron sulfate concentrations of the previous 2 years. Accordingly the H^+ and TDS concentrations decreased and the pH increased.

The residual pyrite content of the lysimeter solids is substantially the same in both the high and low rate lysimeter solids. The time of decrease of TDS in leachate from all lysimeters is approximately the same. This suggests that the pyrite oxidation rate is essentially constant and independent of flushing rate. Hence the main effect of water application rate is to dilute a constant production of iron

sulfate to differing degrees. It is possible that a higher flushing rate does promote a somewhat higher pyrite oxidation rate by keeping the pH at a higher level. There is apparently some evidence that pH's less than 1.5, the pyrite oxidation rate does start to slow down. This may be due to slower kinetics for the Fe^{2+} - Fe^{3+} cycle and its role of attack upon pyrite minerals or a direct effect upon the bacteria. But a 10 times flushing difference in these lysimeters only promotes a small difference in pyrite oxidation rates.

5. The surface 10 cm of the high rate lysimeter has lost 80% of its Ra-226. Taking the average Ra-226 concentration as 122 pCi/g, (see Table 4.5.1, and Appendix A.4) the concentration within the high rate lysimeter is enriched throughout its depth below the surface layer. The loss of Ra-226 from the top of the lysimeter explains the source of the pulse of Ra-226 observed during the last 2 years of lysimeter leaching. The probable mineral controlling Ra-226 is assessed in section 4.5.2; a scenario describing the peak behaviour of Ra-226 is given in Chapter 9.
6. A larger fraction of Ra-226 has been leached from the high rate lysimeter than from the low rate lysimeter (see Table 4.5.1), but overall less than 1% has been lost over the 5.5 years of leaching. The larger loss from the high rate lysimeter results mainly from loss of Ra-226 from the top 10 cm. Due to the lower sulfate concentration of the high rate lysimeter, it is possible to hypothesize that a larger fraction of Ra-226 should have been lost due to dissolution of the Ra-226 containing sulfate precipitate throughout its leaching history. The Ra-226 leachate data before the initiation of the peak (see time 500-1400 days, Figure 1) agrees with this hypothesis. The results from Experiment 4 in which larger amounts of Ra-226 are leached as a function of lower pore water concentrations of sulphate support this hypothesis.
7. The low levels of thorium-230 in the solids are consistent with the residual levels expected in solids after leaching in the leaching pachucas. For example, assuming that 95% of uranium minerals and associated daughters (eg. Th-230), are leached in the pachucas, 5% of 325 pCi/gm or 16.3 pCi/gm should remain. The observed value of Th-230 is 16 pCi/gm.

The residual concentration of Th-228 is somewhat enriched relative to that of Th-232 whereas it is expected that they should be the same. That is, the activity of the radioisotopes should be the same if all Th-228 resulted only from Th-232 decay. Because Th-228 is a daughter of Ra-228 and assuming that Ra-228 has similar chemistry to that of Ra-226, it is probable that significant amounts of Th-228 have ingrown from Ra-228. Hence it is probable that there are two different minerals containing Th-228: the mineral containing Th-232 and the mineral containing Ra-228.

Correlations (not shown herein) have been found between radioisotope concentrations and the pH, conductivity, and TDS of the leachates from each lysimeter. The only consistent pattern was an increase of Th concentrations with increase in TDS (or decrease in pH). This is interpreted to mean that higher proton concentrations in biofilm waters are better able to attack the lysimeter minerals containing residual Th species. That is, thorium in the leachate waters originates from residual minerals not attacked in the leaching pachucas and the thorium concentration is controlled by the acidity of biofilm waters.

8. The particle size distribution of the solids is the same for high and low rate lysimeters. The mean grain size is about 0.25 mm with 95% being between 2 mm and 50 μ m. These solids would be classified as quite coarse. Solids classified by Murray and Moffett (1977) as coarse had only 64% of their total weight between these two sizes. The radium content of the high-rate lysimeter solids (122 pCi/g) is less than the coarse fraction of Murray and Moffett (166 pCi/g). The difference can be explained by the smaller surface area in the coarser solids, assuming a uniform surface concentration of Ra-226 co-precipitated with its parent sulfate.

4.5.2 Examination of Tailings Solids by Scanning Electron Microscope and Mossbauer Techniques

Details of the results of the analysis by these two instruments are given in the appendix. A short summary is given here. Scanning Electron Microscope - Xray Emission technology (SEM-XRE) provides the ability to visually examine the morphology of particles, to obtain knowledge of the major elements making up the particles, and to identify the probable minerals and masses of these minerals. Calculation of the mass of minerals can be made, provided a library of typical minerals is available. Establishment of such a mineral library is required to attain the full potential of the SEM-XRE technology. Mossbauer Spectroscopy provides the ability to differentiate oxidation states of Fe and hence to identify both amorphous (Fe hydroxides) and crystalline minerals (Fe sulphates).

The SEM-XRE analyses shows the following:

1. The host mineral quartz particles (50-100 μm) leave the leaching pachucas partially covered with surface precipitates of size 2-5 μm and smaller. These precipitates have various forms including rods, polygons and dendrites. They are quite porous and flaky, indicating a large surface area. They cover about 5-10% of the total particle surface. These particles are the probable location for formation of secondary, Ra-226 containing, sulfate minerals formed in the leaching pachucas. For this discussion, "precipitates" or "particles" are the terminology used to describe those precipitates.
2. The host mineral quartz solids leaving the partial neutralization tank are essentially completely covered with surface precipitates. Similar characteristics are observed on host quartz solids leaving the final neutralization tank. These precipitates have much Ca and S in them but significant quantities of Al, Si and K are also observed. Part of the Si results from the "background" quantities in host particles; some of the Al-Si and K are found in distinct plate shape particles which are probably primary alumino silicates intermixed with the ore and which are the particles attacked by protons in the lysimeters. Some rods are observed whose composition and morphology are consistent with ettringite (calcium sulfate aluminate hydrate), a

mineral formed during concrete reactions. Hence the existence of ettringite and the relative importance of ettringite and gypsum in the surface precipitates and their subsequent dissolution in the tailings pile requires further assessment.

3. The lysimeter solids have lost most of the surface precipitate covering the host quartz solids. There is less precipitate coating the quartz mineral solids in the surface sections of the lysimeters than in deeper sections. Qualitatively, the surface layers have about the same degree of coating as the leaching pachuca solids. The lower sections have opaque, amorphous-appearing globules whose content of essentially pure silica suggest that they are the amorphous silica ($\text{SiO}_2(\text{s})$) predicted by the analysis of the leachate chemistry.
4. Pyrite particles (cubes 1-2 microns in size) are found in the top and bottom of the high and low rate lysimeters. Surface precipitates ultrasonicated off of the quartz particles show large amounts of pyrite in the upper, middle and lower depths of the high rate lysimeter (L8). These results confirm the residual sulfide measurements made chemically (see Appendix A.4).
5. The depth of penetration of the electron beam is about 1 μm . Penetration of the beam through the particles causes reflection back off of the host quartz particles and, subsequently, an XRE spectra which is dominated by Si. Samples were ultrasonicated to produce particles free from the host quartz. Some success was attained. The small particles are composed of much pyrite, and particles containing Ca, Al, Si, K and S. Some creative further work is required to allow full exploitation of the SEM-XRE technology. Such work would include ultrasonic techniques coupled with separation of the vibrated particles by centrifugation or flotation.

The Mossbauer analyses shows that pyrite is present throughout all depths of the lysimeters. It is possible that ferric minerals are present. If so, they are present in amounts of less than 5% of total iron. Mossbauer analysis for amorphous and crystalline Fe^{3+} forms of iron sulfate (eg. jarosite) is complicated by fact that the doublet peak for FeS_2 (in which Fe is assigned a low spin number of +2) is at approximately the same location on the spectrum and has approximately the same shift as Fe^{3+} . Hence to fully exploit the potential of Mossbauer spectroscopy, removal of pyrite appears to be a useful recommendation. Care would be required to ascertain that significant quantities of

ferric minerals are not found on the surface of the pyrite particles.

4.5.3 Probable Composition of the Surface Precipitate Containing Ra-226

Leaching pachuca solids and solids from section 4 of the high rate lysimeter (L8-4) were mixed with KCl and Na EDTA solutions. The leachates were analyzed for Ra-226 and certain metals. The probable minerals containing Ra-226 suggested by the literature are calcium sulfate, lead sulfate, barium sulfate, and jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$). The KCl solution acts by increasing the solubility of sulfate and hence the tendency for a sulfate to dissolve; K acts by substituting for the 2^+ metal (isomorphic substitution) in the metal sulfate lattice leading to precipitate breaking. NaEDTA can act in two ways. Na may isomorphically substitute for the 2^+ metal leading to precipitate breakup. EDTA increases the solubility of the metal sulfate by rapidly chelating each metal ion which dissolves from the precipitate.

Plots of Ra-226 versus concentration of each of 4 metals is given in Figure 4.5.1 to 4.5.4. The plot of Ra-226 versus Fe (Fig. 4.5.1) is essentially a scattergram. The plots of Ra-226 versus Pb (Fig. 4.5.2) and Ra-226 versus Ca (Fig. 4.5.3) show lesser, but still quite wide, scatter; if the data for the leaching pachuca solids or the lysimeter are taken separately, there appears to be a relationship between Ra-226 and Pb or between Ra-226 and Ca of some degree. For Ra-226 versus Ba (Fig. 4.5.4), the data from both the lysimeter and tailings essentially collapse into the same set, giving a very distinct relationship. These graphs support a conclusion that coprecipitation of Ra-226 with $\text{BaSO}_{4(s)}$ in the leaching pachucus occurs as surface precipitates on the quartz solids and that this precipitate controls the behaviour of Ra-226 in the mill and its initial dissolution in the tailings. The speciation calculations (section A.2) also suggest that $\text{BaSO}_{4(s)}$ precipitation is quite possible.

It is probable that dissolution and reprecipitation of Ba further down in the tailings pile controls its migration behaviour, but the possible coprecipitation of Ra-226 with secondary minerals such as aluminosilicates, amorphous silica and jarosite cannot be ruled out. Recent evidence that jarosite formation is particularly mediated by oxidizing bacterial solutions and Kaimen's observation of 80,000 pCi Ra-226/g of jarosite shows that such associations exist. The significance of secondary mineral formation to Ra-226 migration requires further assessment. This evidence also suggests that while jarosite

formation is thermodynamically possible in the leaching pachucas, its role as a agent influencing Ra-226 behaviour in the mill is much less probable than that assumed by Snodgrass et al (1982) in their generic model. Jarosite formation and Ra-226 incorporation into the secondary precipitate in the tailings pile is a much more probable explanation of Kaiman's observation. It is also possible that Kaimen's observation could be the exception rather than the rule or that the Ra-226 is reversibly adsorbed rather than coprecipitated with jarosite.

Some Ra-226 relationships with Fe, Pb or Ca cannot be completely rejected. The possible of leaching of substantial quantities of these metals from non-sulfate solids by dissolution and complexation of the metal with EDTA and the association of Ra-226 with small quantities of the metals in solid sulfate form is possible. But their significance does not appear to be large.

6.3.1.7 Chemistry of Leachate from Experiment 3

Less complete chemistry is available for the leachate from Experiment 3 than 1 or 2 but it is sufficient to draw inferences about the major geochemical controls on radionuclide levels. During initial flushing of the controls, the pH was about 7.0 and the calcium was about 600-650 mg/L. This is consistent with dissolution of gypsum. The rate of decline of Ca is slow but steady over the 5 year period. By the third year, the iron concentration was starting to increase, reaching its maximum of 10,000 mg/L in year 5 where the calcium concentration had decreased to 400 mg/L. The dramatic increase in iron is mirrored by the decrease in pH. Accordingly, it is concluded that gypsum was dissolving during the whole period and that about 3 years were required to dissolve sufficient gypsum and allow the colonization of T. ferrocanis before pyrite oxidation reactions began to dominate. While sulfate measurements are not available, it is probable that gypsum solubility controls initial lysimeter constituents but iron sulfate and gypsum control constituents at the end.

Because there is little buffering capacity associated with the gypsum system, the iron sulfate system controls the pH. Because the pH should be of the order of two for an iron concentration of 10,000, it is difficult to decide whether significant amounts of carbonate were being dissolved at the end of 1980 without chemical speciation calculations. Because the pH starts at 7, carbonate dissolution should appear to be insignificant throughout the whole leaching history.

The chemistry of the vegetated tailings leachate is essentially the same as the controls. This shows that outside the root zone, tailings characteristics are essentially unaffected by a vegetated cover. The ability of the sludge-vegetation treatment to maintain a viable vegetated cover suggests that the grass can either tolerate an acidic soil or that pyrite oxidation is minimal in the root zone. Because the chemistry of the vegetated tailings leachate follows that of the control, atmospheric oxygen is able to penetrate sufficiently through the vegetated cover to allow pyrite oxidation rates to be the same as in the control.

High concentrations of aluminum and lower concentrations of chromium, copper, nickel, manganese and zinc are observed near the leaching history of the non-fixed tailings (see Table 16). The magnesium concentration starts high and decreases. The aluminum

pattern is consistent with proton attack upon aluminosilicate minerals described for the old tailings of Experiment 1. Unfortunately no data is available to corroborate this mechanism (e.g., K, Na, K, F). Leaching of the other metals is consistent with oxidation of sulfides containing Cu, Ni and Zn and Cr. The pattern of Mg suggests that it is initially present as a $MgSO_4$ which dissolves. Because Mg can also be derived from an aluminosilicate it is possible that some quantities begin to enter the leachate from the same minerals as Al near the end of the leaching history.

The leaching history of the chemfixed tailings shows that dissolution of all metals observed in the controls is inhibited. Measurements are not available, but it is reasonable to assume that most of the leachate is controlled by dissolution of an (Na, K) (silicate, sulfate) as observed in Experiment 2. That the conductivity starts high on (about 12-14 mmho/cm) and decreases rapidly to about 2 mmho/cm within 2 years of placement suggests that most dissolution of significance was complete by 1978. Furthermore, in 1978, the calcium concentration started to increase suggesting that gypsum dissolution was commencing. Because the pH remains at 3 at the end of leaching, either dissolution of gypsum has not progressed adequately to allow pyrite oxidation reactions to commence or the encapsulation process of Chem Fix is still sufficient to prevent pyrite oxidation reactions. Because calcium dissolution is significant, it is more probable that insufficient gypsum has dissolved to allow initiation of pyrite oxidation reactions. This conclusion questions the permanence of the encapsulation procedure. Physical analysis of the lysimeters would confirm or reject this point.

Radioisotope patterns also lend support to the mechanisms described above. In the mill, much of the Ra-226 and all of the Th carried in the mill waters through the mill are brought down in the final neutralization tanks. The Ra-226 patterns are consistent with dissolution of gypsum in the non-fixed tailings. Except for one set of data (growing season 1978), Ra-226 concentrations in the fixed tailings lag those of the non-fixed tailings, increasing to more substantive levels when gypsum dissolution is initiated. All Th species began immediate dissolution such that in the non-fixed tailing most of the leachable Th appears to have left the lysimeters within 5 years. The pH of the lysimeter water is less than seven at all times. Because $Th(OH)_4(s)$ becomes increasingly less stable at pH's less than 7, proton attack upon the $Th(OH)_4(s)$ aids dissolution. It has been previously hypothesize that $Th(OH)_4(s)$ is enmeshed within gypsum in the final

neutralization tanks. If so, it is expected that the Th pattern in the leachate would more closely parallel that of Ca. Because the Th pattern more closely parallels that of H^+ , it is probable that Th exists as a separate hydroxide particle and is only partially enmeshed in gypsum. This permits dissolution of all Th with only minimal gypsum dissolution.

7.3.7 Calculations of Chemical Speciation in Rio Algom Tailings Leachate

An extensive set of calculations are presented in the appendix A.2 describing the probable concentration of different complexes in the leachate from the control lysimeters of old tailings (Experiment 1). More limited data is available herein. Accordingly a few calculations of the controls on pH at the beginning, at the mid way point, and at the end of these experiments is given.

For these calculations TDS values and electroneutrality are used. Then the system controlling the TDS is hypothesized and pH calculations made. If the hypothesized system is correct, then agreement between calculated and observed pH constitutes some validation of the hypothesis.

For the first pore volumes, it is assumed that only gypsum dissolution controls the pH. For the assumption, the predicted pH is 7.0 compared to observed values of 8.1 (Table 21A). Hence it is possible that either less total inorganic carbon is present or some other buffering system is influencing the initial pH.

These calculations (for gypsum) were made assuming that all the TDS is gypsum. Hence the molar Ca^{2+} or SO_4^{2-} concentration is calculated as equal to TDS divided by (40.1 + 96.1). It is somewhat disconcerting that about 24% of the TDS (Ca , SO_4) is predicted to precipitate. Furthermore the $\text{SO}_4^{2-}/\text{TDS}$ ratios for these lysimeter waters early in their operation (i.e. when the pH is 8) have values averaging 0.33 for the continuous systems and 0.34 for the batch systems. The actual value should be 0.7. These values for TDS are higher than the equilibrium solubility concentration of gypsum (about 2400 mg/L). These TDS measurements probably over-estimate the actual TDS. Assuming that at least 2 waters of hydration are formed during evaporation for TDS measurements, the TDS values are high by $2 \times 18 / (2 \times 18 + 40.1 + 96.1)$ or 21%. These waters of hydration are lost from gypsum at 175°C. Factoring these waters of hydration into the calculations mean that the TDS value used for calculating pH should be 21% lower and that only a marginal amount of TDS would precipitate, a condition consistent with leachate being at equilibrium with gypsum.

Predicted pH's are given for the Rio Algom data in Table 21B assuming that when the pH is less than 5, the TDS is an iron sulfate (with an Fe/S ratio of 1:2). During the early

period, calculations agree with observations if it is assumed that no $\text{Fe}(\text{OH})_{3(s)}$ forms. But during the later period (near the end of lysimeter operation), calculations agree with observations only if it is assumed that $\text{Fe}(\text{OH})_{3(s)}$ precipitation occurs.

One might question whether the iron actually leaves the lysimeter in the 2+ or 3+ oxidation state. Parallel calculations to those given above ($\text{Fe}(\text{OH})_{3(s)}$ precipitation is not, or is allowed), given in Table 21B, shows that the pH is predicted to rise substantially above that observed. This suggests that the iron must be essentially in the 3+ state.

The question arises: whether it is reasonable to invoke iron hydroxide precipitation to explain the pH of the lysimeters during the latter stages. The percentage of TDS lost by $\text{Fe}(\text{OH})_{3(s)}$ precipitation is given in Table 21A for those cases in which precipitation is hypothesized to occur. The proportion predicted to precipitate is extremely high in the high rate lysimeters but not unreasonable in the low rate lysimeters. The proportion of iron which is tied up with different complexes is given in Table 21C assuming, or not assuming, iron hydroxide precipitation occurs. The large fraction of iron tied up with soluble hydroxo polymeric forms of iron (Fe^{3+} with OH) in the no precipitation case switch to become an iron hydroxide solid when precipitation occurs. Because the speciation calculations assume thermodynamic equilibrium, it is probable that kinetics rather than thermodynamics actually control the speciation of iron. This would apply particularly in the high rate lysimeter, because it is unlikely that large amounts of iron hydroxide precipitates are continuously carried from the lysimeter. Also the values for TDS are probably high because of the formation of waters of hydration during evaporation for the TDS measurements.

It is concluded that the iron sulfate system can explain the observed TDS and pH patterns of the Rio Algom tailings for pH values in the 2.5-3.3 range but that the kinetics of $\text{Fe}(\text{OH})_{3(s)}$ precipitation and the concentration of intermediate hydroxo polymeric complexes of iron (e.g. $\text{Fe}_2(\text{OH})_2^{4+}$ etc.) are also influential in determining the actual pH. A more involved analysis of Fe^{3+} hydrolysis kinetics and Fe^{3+} polymeric species and more precise data giving the concentration of iron and other major cations and anions is required to give more accurate predictions of pH than are given herein. Problems associated with kinetics and polymeric species will be of much less concern in actual tailings because they are most analogous to the low application rate; kinetics may be of concern as the pH decreases through the range of pH 4 to pH 2.5.

7.5.7 Relationships Between Ra-226 and TDS Leaching Patterns

These Ra-226 patterns (see Section 7.5.5) are interpreted to result from the dissolution patterns of gypsum except for the initial 2 pore volumes. Flushing during the first 2 pore volumes suggest that Ra-226 which is loosely adsorbed comes out first - then the more constant rate results from the dissolution of Ra-226-gypsum forms. The slow rate of change of cumulative radium leached during 100 to 1000 pore volumes corresponds to the period when little gypsum (TDS) is dissolved. The TDS data and SO_4 data (see next section) continue to show no significant increase beyond 1000 pore volumes whereas the Ra-226 starts to rapidly increase. This suggests that the (Ba, Ra) SO_4 surface precipitate presumed to be the precipitate formed in the leaching pachucas and holding the Ra-226 on the host solids is beginning to break down.

Plots of the rates of radium leached/TDS leached versus TDS concentration and of the ratio of radium leached/ SO_4 leached versus sulfate concentration are given in Figures 56A and 56B for these Madawaska leachates. Corresponding plots are given in figures 56C (ratio of Ra-226/TDS) and 56D (ratio of Ra-226/ SO_4) for the Rio Algom tailings. The period used to calculate the cumulative leaching characteristics of Madawaska tailings are the last 300 days of operation whereas the period for the Rio Algom data is the last 500-600 days (i.e. during the period when the leachate water is acidic, pH ca 2.5-3.5). Plots involving both sulfate and TDS concentrations are given to demonstrate that variations in SO_4 /TDS ratios do not prejudice the plots. The TDS of the Madawaska tailings is assumed to be a gypsum while that of the Rio Algom is assumed to be an iron sulfate.

These plots allow one to determine if sulfate concentration has any significant effect upon the leaching patterns of Ra-226; the ratio of mass Ra-226 leached/mass TDS leached normalizes the Ra-226 leaching pattern to that of gypsum. If Ra-226 mobilization is dependent only on the rate of gypsum leaching, the ratio will be essentially the same and independent of sulfate concentration. The plots of the Madawaska tailings show that the ratio of radium leached/TDS (or SO_4) leached is independent of TDS (SO_4) concentration for sulfate values greater than 0.5 mM. But for lower sulfate concentrations, the ratio becomes quite dependent upon sulfate concentration. Whether the ratio continues to be dependent upon SO_4 at concentrations lower than 0.3 mM (e.g. Fig. 56B) or whether it becomes independent at lower (SO_4)

concentrations (e.g. Fig. 56A) equivalent to 25 mg/L TDS is unclear because of the variability in the SO_4 and TDS concentration data. These plots suggest that certain of the lysimeters (the high rate ones near the end of their operation) had reached the stage where the sulfate mineral controlling the Ra-226 concentrations on the solids had started to dissolve, releasing Ra-226. These plots also suggest that the point of dissolution can be explained by solubility considerations of the sulfate mineral (presumed to be $\text{BaSO}_{4(s)}$) and the sulfate concentration of the leachate water.

The plots of Ra-226 leached/TDS (SO_4) leached for the Rio Algom tailings show a different behaviour. The plots suggest that the leaching behaviour is a function of the sulfate concentration in all lysimeters after the acidic conditions are reached. At lower sulfate concentrations, a higher amount is released than at lower sulfate concentrations. Some care must be used in comparing the interpretation of these plots to those for the Madawaska tailings because the TDS here is essentially an iron sulfate rather than calcium sulfate. Hence the absolute values of the leaching ratio (Ra-226/TDS) are not directly comparable. But the conclusions remain that the leaching behaviour is in part a function of the sulfate concentration of the leachate water. The conclusion is further substantiated by data from the old tailings where the Ra-226 was released from the top 10 cm of the high rate lysimeter when the sulfate concentrations became quite low. But because inconsequential amounts of Ra-226 were released from the old tailings until pyrite was nearly exhausted, it is probable that the relationship represented by Figures 56C and D will represent only a small amount of the total leachable Ra-226 from the Rio Algom tailings until pyrite oxidation reactions are complete.

9.0 CONCEPTUAL MODEL OF TAILINGS LEACHING PROCESSES

Four significant experiments have been conducted in this work. Firstly, the leaching products (pH, TDS, radionuclides) have been monitored from old tailings for 5.5 years; these tailings were placed in the tailings pile some 20 years ago. The probable water chemistry of this leachate (major and minor cations and anions) has been assessed. Formation of secondary minerals is suggested after acid attack upon the parent minerals. While this data was conceived as a "control" for experiment 2, it is a more powerful data base when viewed separately. It serves as a useful base for characterizing expected behaviour of tailings during acid reactions and near the end of the acid period when pyrite oxidation is complete.

Secondly, experiment 2 describes expected radionuclide behaviour from a tailings whose composition is a 30% (Ba, Ra) sludge formed from the chemical precipitation of tailings overflow water containing Ra-226. Its leaching behaviour provides evidence for the behaviour of (Ba, Ra) sludges disposed in distinct zones in the milled tailings pile and an indication of the behaviour of $\text{BaSO}_{4(s)}$ solid formed upon the surface of host quartz solids.

Thirdly, experiment 3 provides evidence for leachate behaviour from tailings that were solidified using the "Chem-Fix" technique. It also provides evidence for the length of time that grasses can survive on such tailings and the radionuclide accumulation rates from root zones up to their leaves. Because the solids of the second and third experiments have not been given a final characterization as were those of the first, emphasis is placed herein upon the evidence they provide for management options as opposed to tailings biogeochemical processes. The results of experiment 5 (characterization of the bacteriology of experiments 2 and 3) are treated similarly.

Fourthly, experiment four examined the leaching characteristics of fresh tailings from the Quirke Mine of Rio Algom (Elliot Lake) and from Madawaska. The tailings from Quirke Mine provide evidence for the leaching behaviour of tailings during the first years after placement. Similar evidence is provided by those from Madawaska. The main difference is that the leachate from the Quirke tailings acidified to pH 2 while Madawaska dropped only to a pH of about 5. No samples are available for solids characterization; hence the results are interpreted in the conceptual model cognisant of this limitation.

A conceptual model of the evolution of the tailings through time is given in Figure 9.1. The time history is divided into 4 different periods - (i) tailings characteristics upon placement and the mill processes which control these characteristics, (ii) tailings processes during gypsum dissolution but before acidification starts, (iii) tailings processes during pyrite oxidation, and (iv) tailings processes after completion of pyrite oxidation in surface layers.

When they leave the mill, the milled solids are coated with 3 different forms of precipitates (or layers). These are precipitates formed in the leaching pachucas, the partial neutralization and the final neutralization tank). In the leaching pachucas, uranium, thorium, Ra-226 and Pb-210 are leached along with various metal sulfides. Oxidation of the reduced metals occurs and metal sulfate precipitates form in the leaching pachucas. Due to the similarity in behaviour between Ba^{2+} and Ra-226, one may describe Ra-226 as having an affinity for Ba^{2+} . Data presented in Section 4.5 suggest that Ra-226 is associated with $\text{BaSO}_{4(s)}$ in the leached solids. Hence it is hypothesized that coprecipitation of Ra-226 with $\text{BaSO}_{4(s)}$ occurs readily, removing Ra-226 from solution. Further, the chemical control of the coprecipitation process upon Ra-226, precludes significant quantities entering solution; rather its chemistry is essentially controlled by reactions occurring on the surface of host quartz minerals and other solids in the leaching pachucas. It is leached from its host uraninite and other uranium minerals by proton attack on the structure but it does not migrate far from the surface of the mineral matrix from which it is leached.

Ra^{2+} forms RaSO_4^0 complexes (see Appendix A2) and is rapidly incorporated into a $\text{BaSO}_{4(s)}$ structure. For concentrations of 100 pCi/L Ra^{226} and 1 mg/L Ba^{2+} , there are approximately 10^{-6} orders of magnitude fewer Ra^{2+} molecules than Ba^{2+} molecules present. Accordingly in such solutions, the number density of Ra-226 incorporated into the $\text{BaSO}_{4(s)}$ lattice is so small that significant effects upon crystal growth of $\text{BaSO}_{4(s)}$ are probably small. Because their molecular sizes are quite similar, significant effects upon crystal growth would occur only when the molar ratio of Ra-226/Ba^{2+} is much larger. But at such high concentrations, formation of a $\text{RaSO}_{4(s)}$ may then be possible.

For this conceptual model, it is argued that thorium species are carried through the mill until the final neutralization tank. Pb-210 will form sulfate complexes in the leaching pachucas with other lead species; it may precipitate in the partial neutralization tank

due to the higher portion of total sulphur (S_T) as SO_4^{2-} . Because the actual S_T in the PN is smaller than in the LP, its precipitation may depend upon competition for SO_4^{2-} by Ca^{2+} and Pb^{2+} or the formation of a $(CaPb)SO_4$ coprecipitate. Some thorium species are coprecipitated at the PN step. The thorium concentration on the solids increases incrementally process by process through the mill. Most of the thorium species are hypothesized to precipitate as hydroxides (see speciation of thorium at pH 4-6 in Fig. A.6) and to then be enmeshed in the gypsum - ettringite (Ca-S) precipitates formed in the final neutralization tanks.

All precipitates formed can be viewed as being successive layers. The total layer is only a few μm thick. While the precipitates are conceptualized herein as being a layer, they are, in fact, a fairly porous structure with rods, dendrites and polygons interwoven. Pore spaces are readily discernable under the SEM. If they do not dissolve in the tailings pile, they significantly increase the tailings particulate surface area compared to the surface area of the host quartz solids. Furthermore, because of incomplete covering of the quartz solids, the layers have irregular thicknesses (from nil to substantial thickness). The precipitates coat small particles (e.g., pyrite, alumino-silicate plates) individually, in clusters; they help "cement" small particles to the large coarser quartz solids formed by the milling of the mined silica - ore solids. Disposal of the FN slurry to the tailings pond/pile provide for separation of agglomerations of small diameter, less dense particles from larger, denser quartz particles. The cementation of fine particles to the large quartz particles may explain the concentrations of pyrite etc. observed in coarse tailings.

Upon placement, the data of experiment 9 show that the leaching water remains basic (pH 7) for a substantial period of time. Dissolution of gypsum should give a pH of about 7. (see section 7.7). The amount of calcium oxides and carbonates added in the mill is in excess of that required to neutralize the acidity of the mill water (Snodgrass et. al., 1982). Measurements on the FN solids show that they contain 0.02-0.04% carbonates (see Appendix A.4). Dissolution of $CaCO_{3(s)}$ into a water saturated with respect to P_{CO_2} of air gives a pH of 8.3. Hence both $CaCO_{3(s)}$ and $CaSO_{4(s)}$ dissolution is occurring. The dominant solids dissolved during the time period are hypothesized to be $CaSO_{4(s)}$ with minor amounts of $CaCO_{3(s)}$ dissolving.

During this dissolution process, it is hypothesized that the $Th(OH)_4$ solid originally enmeshed within the gypsum in the final neutralization tank remains on the particles

until the pH falls sufficiently to allow for their dissolution. Because formation of ThF_x and $\text{Th}(\text{SO}_4)_y$ complexes are important, $\text{Th}(\text{OH})_4(\text{s})$ dissolution will be more favoured than if the complexes did not form.

During this time period of gypsum dissolution, Ra-226 enmeshed within the CaSO_4 precipitates are the main source for Ra-226 in the leachate. This idea is supported by the correlations between Ra-226 and TDS in the leachates of Experiment 4.

When sufficient gypsum has dissolved, pyrite grains are exposed to dissolved oxygen and organisms in the film water covering the solids. Atmospheric oxygen penetrating to various depths of the lysimeter between applications or surges of infiltrating water is the main source for oxygen in the tailings waters. Biofilms containing T. ferrocans develop. The actual origins of such bacteria is not specified herein, but the bacterial work of Experiment 5 and of Ritcey and Silver (1980) demonstrate that pyrite oxidizers develop both in tailings fresh from the mill (experiment 3, 4) and in old tailings which are dried and then leached (experiment 1).

As pyrite oxidation develops, the pH starts to decrease. It is hypothesized that the pH is maintained in the 5-7 range as the pyrite-oxidizer community develops and as carbonates are continually attacked. It is probable that the carbonates, if exposed to acid pore waters are rapidly attacked - the rate limiting step for carbonate removal is hypothesized to be the rate of acid production and the rate of exposure of carbonate surfaces to acidic biofilms not the rate of dissolution of $\text{CaCO}_3(\text{s})$. This assumes that some of the carbonates present in the mill are also covered by precipitates in the mill.

As the pH decreases, increased concentrations of sulfate slow down and minimize the rate of dissolution of gypsum. In waters in which the pH is 2-3 and the TDS is 2-3000 mg/L, the pH can be explained by the sum of $\text{Fe}^{3+} + \text{SO}_4$ (mg/L) being equal to the concentration of TDS, the acidity constant for the HSO_4^- complex and the chemical requirement for electroneutrality in the leachate. Hence the quantity of gypsum dissolving is minimal. This then provides for the maintenance of gypsum on solids in the porous zone of tailings until completion of pyrite oxidation reactions as well observed on the lysimeter solids (old tailings) of Experiment 1.

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In older tailings (20-25 years old), pyrite oxidation is not complete; sufficient pyrite remains for pyrite oxidation reactions to continue (see data in A.4). For rainfall rates (water application rates) which are smaller than normal precipitation, biofilm reactions allow Fe^{3+} and SO_4^{2-} to build up to cause pH's in the range of 0.8-1.0. At higher application rates, the pH's are higher because the continual dilution of biofilm waters by percolating "rainwaters" decreases the Fe^{3+} , SO_4^{2-} and H^+ concentrations. In these waters, electroneutrality is dominated by $\text{Fe}(\text{SO}_4)^+$ and $\text{Fe}(\text{SO}_4)_2^-$ complexes.

Weathering reactions also become important. Analysis of leachates from the old tailings demonstrate that Al, K, Si and Mg concentrations are present in significant amounts (see A.2). These elements originate from proton attack upon aluminosilicates. Plate-shaped, 10 micron particles (see B.1) are probable sources for these elements. The examination of metal ratios and concentrations of metals in the leaching water show that Al, K and Si are retained in the solids, assuming that Mg is conservative. The concentration of Si suggests that the formation of amorphous $\text{SiO}_{2(s)}$ and its solubility in water, controls the Si concentration. While the formation of $\text{Fe}(\text{H}_2\text{SiO}_4)_x$ complexes is possible, their concentration does not appear to be significant. Al and K may be coprecipitated in amorphous $\text{SiO}_{2(s)}$ or in secondary K-aluminosilicates. The large variation of ratios of Al-K-Si in the various precipitates on the host quartz solid suggests that a large number of different secondary precipitates form.

The Fe and S ions formed from pyrite oxidation reactions may all be leached from the tailings. The possibility for reprecipitation of Fe^{3+} and SO_4^{2-} in minerals such as jarosite is thermodynamically possible, particularly in the low rate lysimeters where the saturation index is large (see A.2). Such formations will most likely be observed in solutions containing T. ferrocanis. Above pH 2, $\text{Fe}(\text{OH})_{3(s)}$ is predicted to form rapidly (see A.2). But the Mossbauer analysis (see B.1) indicate that the quantity of Fe^{3+} minerals such as jarosite is 5% in all samples analyzed (mill and lysimeters). Hence it is probable that most of the Fe and SO_4 escapes with the leachate waters and that the colour in the lysimeter solids (see A.4) attributed to $\text{Fe}(\text{OH})_{3(s)}$ represents a very small quantity of total iron.

When the pH is below about 3 in both experiment 1 and 4, the TDS is dominated by Fe and SO_4^{2-} . While the oxidation state of Fe_T is not precisely defined because leachate samples analyzed herein have been stored for 1-2.5 years, an assumption that essentially

all the Fe is as Fe^{3+} is justified by the electroneutrality balance for the old tailings (see A.1) and for predictions of pH for the new tailings of experiment 4 (Appendix C1).

It is estimated that measurements of TDS are too high by about 20% in calcium sulfate waters and 30% in iron sulfate waters. This is attributed to 2 waters of hydration not being removed from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ during evaporation of the calcium sulfate water and to about 1/3 of the 6 waters octahedrally - coordinated to Fe^{3+} not being lost during evaporation (drying 100 mL of water at 105°C for 1-hr). For the calcium sulfate water, this error brings the TDS measurements into agreement with TDS predicted by the solubility product for gypsum (approximately 1.8×10^{-4}). Note this solubility product predicts approximately 1700 mg/L TDS if activity corrections are ignored and approximately 2400 mg/L when activity corrections are included). The waters of hydration of gypsum are lost in the $150\text{--}175^\circ\text{C}$ range. For iron sulfate, anions + cations balance with TDS measurements when volatile dissolved solids (VDS) are included (see A.1). VDS are assumed to be waters of hydration associated with Fe^{3+} . Accordingly TDS values measured during the experiments must be decreased by approximately 30% when the pH is less than 3.5-4 to give an accurate measurement of the TDS which has been lost from the tailings with the leachate.

The source of Ra-226 during the time that the leachate is acidic requires some explanation. Dissolution of small amounts of $\text{Ba}(\text{SO}_4)_s$ is possible. Dissolution of residual gypsum minerals containing Ra-226 is possible. The high sulfate concentrations argue against such dissolution.

One possible source of the Ra-226 in addition to precipitates is the same as that of Th-230 - the residual uranium minerals containing Th-230 and Ra-226. The quantities of Th-230 and Ra-226 leached respectively are 0.084 and 0.0021 micro Ci from the low rate lysimeter and 0.15 and 0.085 micro Ci from the high rate lysimeter. Much of the Ra-226 in the high rate lysimeter is derived from the pulse near the end of leaching and not from the long-term steady rate of leaching. The leachate chemistry shows that the thorium concentrations (Th-230, Th-232 and Th-228) increase as the pH decreases. This suggests that residual minerals containing thorium are attacked by protons and that the residual minerals are the main source of thorium in the leachate from the old lysimeters. It can be assumed that similar quantities of Th-230 and Ra-226 are found in these residual minerals, which remain after the leaching pachucas. Hence if Th-230 is liberated by

weathering (H^+ from pyrite oxidation), it is expected that Ra-226 would likewise be liberated.

But $BaSO_4(s)$ is calculated to form in the biofilms. These biofilms have higher concentrations of Fe and SO_4 than the percolating leachate. Because the mass of Ra-226 leached is significantly less than that of Th-230 during the 5.5 years of leaching, it is concluded by this author that the Ra-226 and Th-230 are released by proton attack on residual minerals containing these radioisotopes but that much of Ra-226 liberated is retained by coprecipitation reactions with $BaSO_4(s)$ and/or secondary aluminosilicates and amorphous $SiO_2(s)$.

At the conclusion of significant production of sulfate from pyrite oxidation reactions, the Ra-226 containing coprecipitate on the host quartz mineral particles begins to dissolve due to the low sulfate concentration in the pore water. The dissolution occurs at the top of the tailings (see A.4 for solids data). It is estimated that 80% of Ra-226 is dissolved in 1.5 years (the time of the Ra-226 peak from the high rate lysimeters) from 10 cm of tailings. The subsequent behaviour of the high rate lysimeters suggests that this does not occur continuously. The Ra-226 appears to have reprecipitated in lower depths of the tailings because this mass has not left the tailings. Reprecipitation is probable, but why the peak declines is not known. It is hypothesized that local variations in deeper zones of the tailings provide large enough concentrations of sulfate to prevent continuous dissolution of $BaSO_4(s)$.

With respect to tailings management strategies, experiment 2 shows that higher Ra-226 concentrations percolate from (Ra, Ba) SO_4 sludge deposits. Lack of water chemistry samples at present preclude substantive arguments about Ba^{2+} -Ra-226 relationships in leachate for these lysimeters. But these lysimeters could provide valuable data on the solubility controls of $BaSO_4$ in water percolating through acid tailings. Samples from near the bottom of the $BaSO_4(s)$ sludges (above the tailings) and at the bottom of the tailings of lysimeters of experiment 2 would provide valuable insight into the behaviour of Ra-226 and $BaSO_4(s)$ in acid tailings. Characterization of these sludge solids (Experiment 2), restarting these lysimeters (Experiment 2) and the old tailing samples (Experiment 1) would provide 2 sets of data which could better define the Ra-226 behaviour under the influences of $BaSO_4(s)$ precipitation-dissolution reactions. Of particular utility would be data from the high rate lysimeters (Experiment 1) because

these lysimeters appear to be on the verge of continually losing their Ra-226. Complete metal scans on leachate should be measured occasionally in addition to radionuclides, TDS and pH; Ba should be measured routinely if these lysimeters are restarted.

The results of Experiment 3 show that grasses can grow in tailings to which neutralizing agents (e.g., "Chem Fix") are added. These agents are assumed to be chemical precipitates. But if dissolution of this precipitate is then sufficient to allow exposure of pyrite grains to the atmosphere, acidity reactions can be initiated. These reactions may become of sufficient magnitude to poison vegetative growth if the grasses are not able to maintain more neutral conditions about their root zone. The key to avoiding acidity reactions is the ability of the fixing agent to maintain a coating over the pyrite particles.

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TABLE A. 1a

DESCRIPTION OF LEACHATE SAMPLES ANALYZED

Water ⁺	IEC BEAK Sample No.	Period Sampled	Date Sampled from Lysimeter	Lysimeter Sample Volume	WTC Analysis		Description of Sample Condition (Jan. 1983)	
					TDS (mg/L)	pH	pH	Visual
1	28	32	Dec. 79-Apr. 80	L1 50	215	0.7	1.1 ^x	slightly cloudy; dark amber
	29	33	Apr. 80-Aug. 80	L1 1000	166	1.2	1.2	slightly cloudy; brown
	30	34	Aug. 80-Jan. 81	L1 1000	63	1.4	1.3	slightly cloudy; dark amber-contains remains of some Tiferrocans
2	31	36	Apr. 81-Aug. 81	L1 1000	26.8	1.5*	1.5	slightly cloudy, amber
3	32	32	Dec. 79-Apr. 80	L7 1000	187	0.8	1.3	dark brown
	33	32	Dec. 79-Apr. 80	L7 150	187	0.8	1.1 ^x	dark brown
	34	32	Dec. 79-Apr. 80	L7 750	187	0.8	1.4	dark brown
4	35	33	Apr. 80-Aug. 80	L7 1000	126	1.0	1.4	brown
	36	34	Aug. 80-Jan. 81	L7 1000	61.6	1.2	1.5	clear, amber
	37	35	Jan. 81-Apr. 81	L7 1000	27.3	1.5	1.7	clear, amber; some bacterial remains
5	38	36	Apr. 81-Aug. 81	L7 1000	29.9	1.5*	-	clear, amber; some bacterial remains
6	39	32	Dec. 79-Apr. 80	L2 50	1.5	2.3	1.5 ^x	clear, colourless
	40	33	Apr. 80-Apr. 80	L2 500	.778	2.5	2.4	clear, colourless
	41	33	Apr. 80-Aug. 80	L2 1000	.778	2.5	1.6 ^x	clear, colourless, some bact. remains
7	42	34	Aug. 80-Jan. 81	L2 1000	.443	2.6	2.2	clear, colourless except for reddish-orange specs
	43	35	Jan. 81-Apr. 81	L2 450	.222	3.0	1.7 ^x	clear, colourless
	44	35	Jan. 81-Apr. 81	L2 500	.222	3.0	1.9 ^x	clear, colourless
8	45	36	Apr. 81-Aug. 81	L2 1000	.10	3.2*	2.0 ^x	clear, colourless
9	46	32	Dec. 79-Apr. 80	L8 75	1.2	2.3	1.6 ^x	clear, colourless
	47	33	Apr. 80-Aug. 80	L8 1000	.502	2.5	2.1	clear, colourless
	48	33	Apr. 80-Aug. 80	L8 1000	.502	2.5	2.2	clear, colourless
	49	34	Aug. 80-Jan. 81	L8 1000	.483	2.5	1.8 ^x	clear, colourless
10	50	36	Apr. 81-Aug. 81	L8 1000	.150	3.1*	-	clear, colourless

* data not recorded, value is average of period 35 and 37

+ waters used for speciation calculations, section A.2

x samples to which HNO₃ is added as preservative

TABLE A.1(b) Chemistry of Leachate Waters (Units: millimoles/L unless states otherwise)

SAMPLE NO.	Al	Si	Ca	Ca	Ca	Co	Cu	Fe	K	Mg	Mn	Ni	Pb	Tl	Ti	V	Zn	Zr	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻²
		(µM/L)			(µM/L)							(µM/L)	(µM/L)	(µM/L)								
T 1120	31.4	.42	3.39	1.4	.714	.538	953	857	1.10	30.6	174	8.93	10.6	.420	.0448	.0207	.109	.42	.04	49.4	1290	
29	17.1	.39	1.47	3.5	.602	.545	673	5.09	.691	21.3	140	10.1	7.08	.278	.0553	.076	.0509	.68	.44	.08	971	
30	3.53	.20	.577	1.9	.14	.394	245	.639	.121	2.65	64.7	11.6	.733	.0512	.00987	.0045	.0067	.08	1.01	.08	370	
31	.83	.12	.377	.60	.0020	.301	89.7	.128	.0173	1.8	25.7	11.1	.257	.0132	.00318	.0049	.0011	.03	.06	.06	183	
32	2.2	.39	.546	2.0	.635	.395	770	5.19	.744	23.1	184	10.9	7.11	.276	.0379	.0178	.0553	.29	4.01	.08	1060	
33	20.6	.39	.671	2.0	.584	.405	791	5.42	.701	23.8	152	11.1	6.94	.286	.051	.0178	.0559	.553	4.15	54.8	1090	
34	20.1	.39	.586	2.9	.609	.397	754	5.24	.749	22.9	167	10.4	7.03	.282	.0347	.0187	.0555	.47	3.78	.08	1060	
35	1.15	.30	.717	2.7	.428	.423	485	2.43	.342	13.3	106	12.8	3.41	.132	.0210	.013	.0232	.37	3.24	.08	703	
36	3.18	.20	.134	2.2	.210	.340	238	.691	.109	5.8	61.0	11.6	.60	.0482	.0104	.0090	.0061	.11	2.03	.08	337	
37	.86	.12	.624	.90	.0872	.233	105	.103	.0230	2.0	26.9	9.65	.04	.0141	.00411	.0043	.0013	.03	1.52	.08	167	
38	.76	.11	.0312	.04	.064	.244	84.5	.0512	.018	1.5	28.1	8.69	.17	.00875	.00388	.014	.006	.022	.786	.08	185	
39	.11	.20	.0472	.04	.0058	.087	4.26	.0767	.0086	4.9	1.97	13.8	.04	.00228	.0001	.0009	.006	.03	.385	41.4	64.5	
40	.10	.24	.0170	.04	.0039	.078	2.22	.102	.0053	5.1	1.2	15.0	.09	.00089	.0002	.0008	.006	.03	.14	.08	440	
41	.10	.24	.0457	.04	.0041	.0181	2.40	.0767	.0053	4.7	1.5	15.0	.09	.00089	.0001	.0008	.006	.03	.17	15.4	3.90	
42	.057	.26	.0465	.09	.0020	.016	.371	.0767	.0045	5.3	1.0	17.6	.04	.0048	.0021	.0008	.006	.03	.375	.08	2.91	
43	.035	.55	.067	.04	.0009	.0088	.218	.0767	.0045	5.3	0.9	21.0	.04	.00065	.0004	.0008	.006	.03	.459	16.3	.65	
44	.034	.55	.0120	.04	.001	.00705	.229	.0767	.0033	5.1	0.9	20.3	.04	.0008	.0001	.0008	.006	.03	.388	13.2	.67	
45	.032	.65	.057	.09	.0009	.00801	.0711	.128	.0053	5.3	0.9	4.83	.04	.0003	.0001	.0008	.006	.03	.113	16.6	.59	
46	.10	.20	.0150	.09	.0051	.0068	3.21	.102	.0046	5.5	1.9	14.7	.09	.0011	.0001	.0008	.006	.03	.385	34.2	5.55	
47	.11	.24	.057	.09	.0024	.0013	1.40	.128	.0053	4.9	1.0	14.5	.09	.00083	.0001	.0008	.006	.03	.112	.08	440	
48	.11	.24	.012	.09	.0032	.002	1.40	.128	.0008	5.3	1.4	15.0	.09	.00079	.0001	.0008	.006	.03	.122	.08	432	
49	.11	.20	.0150	.09	.0027	.0010	.790	.102	.0045	5.3	0.9	13.8	.09	.00058	.0001	.0008	.006	.03	.14	20.8	1.81	
50	.04	.37	.003	.09	.0009	.0003	.061	.002	.002	0.2	0.9	11.3	.04	.0001	.0001	.0008	.006	.03	.15	16.6	1.07	

TABLE A. 2

Fe:S RATIO AND ELECTRONEUTRALITY BALANCE FOR LEACHATE FROM OLD TAILINGS

Sample No.	Description	Ratio per/(SO ₄) _T	Σ Anions** (meq/L)	Σ Anions*** (meq/L)	Σ Cations (based on Fe ²⁺)	Σ Cations (based on Fe ³⁺ +X meq/L)
28	L1-Low	0.748	2560		2110	3060
29	L1-Low	0.693	1940		1530	2200
30	L1-Low	0.662	742		567	812
31	L1-Low	0.674	267		215	305
32	L1-Low	0.726	2120		1660	2430
33	L7-Low	0.726	2190		1670	2460
34	L7-Low	0.711	2120		1610	2370
35	L7-Low	0.690	1400		1040	1530
36	L7-Low	0.706	676		520	758
37	L7-Low	0.629	331		234	339
38	L7-Low	0.484	370		258	348
39*	L2-High	0.654	13.3		-	4.3
40	L2-High	0.505	8.97		9.0	11.2
41*	L2-High	0.615	8.00		14.9	17.3
42	L2-High	0.132	6.01		7.4	7.8
43*	L2-High	0.257	2.18		4.0	4.2
44*	L2-High	0.342	1.71		0.6	0.8
45*	L2-High	0.080	1.34		-6.2	-6.1
46*	L8-High	0.578	11.5		-7.2	-4.7
47	L8-High	0.318	9.11		11.3	12.7
48	L8-High	0.324	8.88		9.7	11.1
49*	L8-High	0.281	5.77		2.0	-1.9
50*	L8-High	0.042	2.51		13.3	-3.5

* Substantial quantity of HNO₃ was added to sample. The measured (NO₃⁻) and associated H⁺ was subtracted from values for Σ anions and Σ cations respectively.

** Based upon assuming all sulfate as SO₄²⁻.

*** Based upon calculating actual speciation of SO₄²⁻ with H⁺

TABLE A.3:

pC total for

#	MET INIT.	WATER					NUMBER				
	GUES.	1	2	3	4	5	6	7	8	9	10
20	AL 2.	1.5	3.08	1.69	2.04	3.13	3.96	4.24	4.5	4.0	4.5
10	BA 7.	6.38	6.92	6.41	6.52	7.0	6.7	6.6	6.2	6.7	6.4
1	CA 3.5	2.46	3.4	3.26	3.53	4.51	4.33	4.78	4.8	4.6	5.5
11	CD 7.	6.85	6.1	5.7	5.54	7.05	7.05	7.0	7.0	7.0	7.0
17	CO 5.	3.15	4.066	3.2	3.37	4.07	5.24	5.7	6.0	5.3	6.0
9	CU 4.3	3.27	3.52	3.4	3.37	3.61	4.73	4.9	5.1	4.8	5.3
6	FE 3.0	.0186	1.047	.114	.314	1.048	2.375	3.431	4.327	2.493	4.346
4	K 3.0	2.07	3.89	2.28	2.614	4.29	4.12	4.12	3.89	4.0	4.3
2	MG 3.5	2.96	4.76	3.13	3.44	4.74	5.07	5.3	5.3	5.2	5.7
8	MM 5.0	4.51	5.75	4.64	4.88	5.82	5.31	5.3	5.3	5.3	6.7
5	NA 5.0	3.52	4.4	3.76	4.06	5.0	5.0	5.0	5.0	4.3	5.0
13	NI 6.0	3.76	4.59	3.74	3.97	4.55	5.7	6.0	6.0	5.7	6.0
15	PB 5.0	5.04	4.95	4.96	4.89	5.06	4.9	4.8	5.32	4.83	4.95
31	TH 7.0	2.63	3.4	2.8	3.5	4.0	4.9	5.0	5.3	5.3	5.3
25	TI 5.0	3.38	4.88	3.56	3.88	5.0	5.6	6.3	5.9	6.0	7.0
12	ZN 5.0	4.69	5.3	4.75	4.89	4.5	6.0	6.1	6.1	6.1	6.1
35	RA 12.0	13.5	12.8	13.2	13.	12.8	12.2	11.9	11.7	12.	11.7
4	P 4.5	3.38	4.52	3.54	3.434	4.66	4.5	4.5	4.5	4.5	3.66
3	CL 3.0	4.85	3.07	2.4	2.49	3.53	3.4	3.4	3.94	3.4	3.82
2	SO 2.	.107	.885	.0253	1.53	.745	2.19	2.55	3.23	2.255	2.971
50	H+	0.7	1.5	0.8	1.0	1.5	2.3	2.55	3.2	2.4	3.1

TABLE A.4: PERCENTAGE OF METAL/LIGAND BOUND WITH BINDING COMPLEX

Metal/ Ligand	Bound With	Water No.										
		1	2	3	4	5	6	7	8	9	10	4*
Al	Free	77.4	34.0	55.7	47.7	23.0	36.2	28.1	21.9	35.2	25.4	98.5
	with F	0.6	1.2	0.7	1.8	0.9	17.4	40.4	67.9	220	530	0.7
	with SO ₄	22.	64.8	43.6	50.5	76.1	46.3	31.3	9.0	42.5	20.8	0.8
	with OH	-	-	-	-	-	-	-	1.2	-	0.8	-
Ba	Free	83.3	67.3	31.0	31.9	50.7	81.6	84.6	99.4	83.0	798	99.7
	with SO ₄	9.5	32.7	10.2	13.2	39.8	18.4	15.4	5.6	17.0	10.0	-
	as BaSO ₄ (s)	7.2	-	58.8	54.9	9.5	-	-	-	-	10.2	-
Ca	Free	89.7	67.3	75.2	70.8	56.0	81.6	84.6	94.4	83.0	88.9	99.7
	with SO ₄	10.3	32.7	24.8	29.2	44.0	18.4	15.4	5.6	17.0	111	-
Cd	Free	89.4	63.5	66.8	62.7	51.1	79.1	81.9	93.3	80.9	87.3	93.9
	with Cl	-	3.1	7.1	6.7	0.7	2.7	3.0	1.1	2.2	1.7	5.8
	with SO ₄	10.6	33.4	26.1	30.6	48.1	18.1	15.7	5.6	16.9	11.0	-
Co ³⁺	Free	100	99.8	99.9	99.9	99.7	99.0	53.7	0.9	66.1	2.3	100
	with F	-	-	-	-	-	0.9	1.2	-	0.7	-	-
	as Co(OH) ₃ (s)	-	-	-	-	-	-	45.0	99.1	33.1	97.6	-
Ca ²⁺	Free	89.7	67.2	75.0	70.6	56.0	81.6	84.5	94.3	82.9	88.8	99.5
	with SO ₄	10.3	32.7	24.8	29.2	44.0	18.4	15.4	5.6	17.0	11.1	-
Fe ³⁺	Free	26.0	5.2	12.2	9.3	3.3	4.3	4.0	-	2.6	1.7	72.1
	with F	-	-	-	-	-	-	0.6	-	-	-	-
	with SO ₄	72.0	92.1	86.3	89.6	95.2	53.6	43.7	1.9	30.3	13.4	5.9
	with OH as Fe(OH) ₃ (s)	1.9	2.6	0.8	1.0	1.5	27.1	51.7	41.6	22.6	84.6	21.5
K	Free	98.8	96.2	95.5	94.9	93.0	98.9	99.2	99.8	49.0	49.5	100
	with SO ₄	1.2	3.8	4.5	5.1	7.0	1.1	0.8	-	1.0	-	-
Mg	Free	91.7	72.1	79.2	75.3	61.6	84.8	87.4	95.5	86.0	90.9	99.8
	with SO ₄	8.3	27.9	20.8	24.7	38.4	15.2	12.6	4.5	14.0	9.1	-
Mn	Free	89.7	67.1	74.7	70.3	56.0	81.4	84.4	94.3	82.8	88.7	99.2
	with Cl	-	-	0.6	0.6	-	-	-	-	-	-	-
	with SO ₄	10.3	32.6	24.7	29.1	44.0	18.3	15.4	5.6	17.0	11.1	-
Na	Free	99.0	97.0	96.4	95.9	94.0	99.1	99.3	99.8	99.2	99.6	100
	with SO ₄	1.0	3.0	3.6	4.1	5.6	0.9	0.7	-	0.8	-	-
Ni	Free	89.7	67.2	75.0	70.6	56.0	81.6	84.5	94.3	82.9	88.8	99.6
	with SO ₄	10.3	32.7	24.8	29.2	44.0	18.4	15.4	5.6	17.0	11.1	-

IEC bank

Pb	Free	77.6	44.7	53.7	48.3	33.6	63.4	68.1	86.6	65.6	75.7	97.3
	with Cl	-	0.7	1.8	1.6	-	0.7	0.8	-	0.6	-	1.9
	with SO ₄	22.4	54.6	44.5	50.1	66.3	35.9	31.1	13.0	33.8	23.8	0.7
Th	Free	1.0	-	-	-	-	-	-	-	-	-	43.3
	with F	-	-	-	-	-	0.7	3.4	33.4	1.0	9.4	-
	with SO ₄ with OH	98.9	99.9	99.7	99.8	100.0	99.2	96.5	66.3	99.0	90.5	51.2
TiO ²⁺	Free	84.6	56.3	65.6	60.4	44.5	73.7	77.6	4.4	75.5	75.9	99.5
	with SO ₄	15.4	32.7	34.6	39.6	55.5	26.3	22.4	-	24.5	15.1	-
	as TiO(OH) ₂ (s)	-	-	-	-	-	-	-	95.2	-	9.1	-
Zn	Free	89.7	67.3	75.2	70.7	56.0	81.6	84.6	94.4	83.0	88.9	99.7
	with SO ₄	10.3	32.7	24.8	29.2	44.0	18.4	15.4	5.6	17.0	11.1	-
Ra	Free	31.4	17.7	9.7	8.6	9.6	57.8	67.1	89.8	61.2	76.9	96.4
	with SO ₄	68.6	82.3	90.3	91.4	90.4	42.2	32.9	10.2	38.8	23.1	3.6
F	Free	-	-	-	-	-	-	0.9	1.4	0.6	1.3	-
	with Al ³⁺	43.5	32.1	48.9	43.5	31.0	65.8	88.5	89.0	79.6	93.8	16.2
	with Fe ³⁺	55.6	66.0	50.4	55.7	66.0	31.8	6.9	-	18.0	0.7	79.1
	with Th with H	0.7	1.3	-	0.6	-	-	1.6	8.8	-	3.3	4.6
Cl	Free	-	-	-	-	2.5	1.5	2.0	0.7	1.4	1.0	-
	with Fe ³⁺	51.9	97.4	81.8	88.3	98.7	99.8	99.4	100	99.9	100	40.0
SO ₄	Free	48.1	2.6	18.2	11.6	1.2	-	-	-	-	-	60.0
	with Al	0.9	12.9	3.8	5.7	21.9	50.4	81.3	94.7	70.3	92.9	0.5
	with Fe	1.0	0.5	1.2	0.9	-	0.8	0.7	-	0.8	0.6	-
	with Th	92.7	72.6	83.0	80.8	59.3	36.3	6.0	-	18.5	0.6	97.3
	with H	0.5	0.6	-	-	-	-	0.6	0.9	-	0.7	0.6
		4.9	13.2	11.6	12.4	18.2	11.3	11.0	3.3	9.9	4.8	1.4

Note: 4* contains the actual pSO₄²⁻ measured analytically. Other calculations for pE etc. are made using water 4, not 4*

TABLE A.5: PERCENTAGE OF METAL/LIGAND BOUND IN COMPLEXES

a) Iron/Sulphate

Metal/ Ligand	Bound With	Water No.								
		1	2	3	4*	5	6	7	8	9
Fe pE=13	Free Fe ³⁺	22.9	5.2	11.5	62.9	3.2	4.2	3.9	1.9	2.5
	Fe ³⁺ with SO ₄	70.3	90.0	85.4	5.8	94.0	52.6	42.1	42.1	31.1
	Fe ³⁺ with OH	1.6	2.6	0.8	17.1	1.5	26.6	51.0	-	22.7
	Fe ³⁺ as (Fe(OH) _{3(s)})	-	-	-	-	-	13.8	-	55.2	42.2
	Free Fe ²⁺	4.6	1.5	1.6	13.8	0.7	2.1	2.1	-	1.1
	Fe ²⁺ with SO ₄	0.6	0.7	0.6	-	0.6	-	-	-	-
SO ₄ pE=13	Free	1.1	13.5	3.9	0.6	21.7	50.5	81.2	94.6	68.8
	with Al	1.1	0.5	1.2	-	-	0.8	0.7	-	0.9
	with Fe ³⁺	91.0	71.2	81.4	95.9	58.9	36.1	5.8	-	19.1
	with Fe ²⁺	0.7	0.5	-	0.8	-	-	-	-	-
	with Th	0.5	0.6	-	0.6	-	-	0.6	0.9	-
	with H	5.5	13.5	12.1	1.7	18.5	11.6	11.2	3.4	10.7

b) Iron/Sulphate

Metal/ Ligand	Bound With	pE = 12 Water No.						pE = 10 Water No.				
		1	2	3	4*	5	6	1	2	3	4	5
Fe pE=12	Free Fe ³⁺	12.4	4.6	8.1	31.7	3.3	4.2	-	0.9	0.6	1.4	0.9
	Fe ³⁺ with SO ₄	59.6	76.0	74.9	5.2	83.3	44.9	6.1	11.4	22.7	0.9	15.8
	Fe ³⁺ with OH	0.7	2.0	0.5	5.8	1.5	27.1	-	-	-	-	-
	Fe ³⁺ as Fe(OH) _{3(s)}	-	-	-	-	-	-	-	-	-	-	-
	Free Fe ²⁺	22.5	11.4	11.5	56.4	6.6	19.2	54.1	62.4	42.1	94.6	55.6
	Fe ²⁺ with SO ₄	4.8	5.9	4.9	-	5.3	4.3	39.5	25.0	34.5	0	27.5
SO ₄ pE=12	Free	2.0	17.3	4.9	1.9	24.2	52.9	6.3	54.8	16.5	19.3	58.8
	with Al	1.6	0.5	1.4	-	-	0.8	3.9	0.6	2.9	2.0	-
	with Fe ³⁺	80.1	61.1	73.8	85.2	52.9	30.9	9.5	10.5	28.1	15.5	11.1
	with Fe ²⁺	5.9	4.1	4.0	7.2	2.6	2.8	48.4	17.2	28.1	44.4	13.7
	with Th	0.5	0.6	-	0.8	-	-	0.6	0.6	-	1.6	-
	with H	9.7	16.2	15.4	4.4	19.7	11.8	31.0	16.2	23.9	17.2	15.8

c) Metal/Ligand

Metal	Bound With	pE=12 Water No.					pE=10 Water No.				
		1	2	3	4A	5	1	2	3	4A	5
Al	Free with F with SO ₄	65.7	35.3	48.7	97.2	24.9	28.3	37.7	16.9	90.6	29.9
		0.8	1.3	0.8	1.2	1.0	1.2	2.6	1.1	3.4	1.9
		33.5	63.4	50.5	1.6	74.1	70.4	59.7	82.0	6.0	68.2
Ba	Free with SO ₄ BaSO ₄ (s)	44.7	63.9	23.8	99.2	50.2	13.1	71.4	12.5	97.2	66.9
		9.5	33.1	10.2	0.8	39.8	9.5	28.6	10.2	2.8	33.1
		45.7	3.0	66.0	-	9.9	77.4	-	77.3	-	-
Ca	Free with SO ₄	82.4	65.9	69.9	99.2	55.8	57.8	71.4	55.0	99.2	66.9
		17.6	34.1	30.1	0.8	44.2	42.2	28.6	45.0	2.8	33.1
Mg	Free with SO ₄	85.5	70.9	74.5	99.4	61.4	63.3	75.8	60.6	97.8	71.8
		14.5	29.1	25.5	0.6	38.6	36.7	24.2	39.4	2.2	28.2
Pb	Free with Cl with SO ₄	65.1	43.2	47.4	96.2	33.4	35.3	49.7	32.6	92.4	44.6
		-	0.6	1.5	1.9	-	-	-	-	1.0	-
		34.9	56.2	51.1	1.9	66.5	64.7	50.1	67.0	6.6	55.4
Th	with SO ₄	99.5	99.9	99.8	64.6*	100.0	99.9	99.9	100.0	91.4	99.9
Zn	Free with SO ₄	82.4	65.9	69.9	99.2	55.8	57.8	71.4	55.0	97.2	66.9
		17.6	34.1	30.1	0.8	44.2	42.2	28.6	45.0	2.8	33.1
Ra	Free with SO ₄	17.9	14.4	7.8	88.4	9.3	6.4	10.6	5.3	61.6	8.1
		82.1	85.6	92.2	11.6	90.7	93.6	89.4	94.7	38.4	91.9

*Remainder is free

TABLE A.6: SPECIATION CALCULATIONS FOR WATER 1*

Metal/Ligand	Bound with	Percentage in Complex at pH					
		0.1	0.3	0.5	0.7	1.0	1.5
Fe ³⁺	Free	2.9	2.6	2.2	1.9	1.5	1.2
	with SO ₄	97.0	97.3	99.7	98.0	98.3	98.0
	with OH	-	-	-	-	-	0.8
	with Fe(OH) _{3(s)}	-	-	-	-	-	-
SO ₄	Free	1.0	1.4	1.8	2.1	2.6	3.0
	with Al	-	0.5	0.5	0.6	0.6	0.6
	with Fe ³⁺	80.2	84.3	87.4	89.9	92.4	94.7
	with Th	-	-	-	-	-	-
Al	with H	18.2	13.7	10.2	7.3	4.3	1.6
	Free	20.0	17.7	15.0	12.7	10.6	8.6
	with F	-	-	-	-	-	-
	with SO ₄	79.7	82.0	84.7	86.9	89.1	91.1
Ba	Free	9.1	8.1	7.2	6.5	5.7	4.9
	with SO ₄	9.5	9.6	9.6	9.6	9.6	9.6
	as BaSO _{4(s)}	81.4	82.3	83.2	83.9	84.7	85.5
	Free	48.7	46.0	43.1	40.6	37.4	34.1
Ca	with SO ₄	51.3	54.0	56.9	59.4	62.6	65.9
	Free	54.5	51.7	48.8	46.2	42.9	39.5
	with SO ₄	45.5	48.3	51.2	53.8	57.1	60.5
	Free	27.4	25.3	23.2	21.4	19.2	17.1
Pb	with Cl	-	-	-	-	-	-
	with SO ₄	72.6	74.7	76.8	78.6	80.8	82.9
	Free	100.0	100.0	100.0	100.0	100.0	100.0
	with SO ₄	-	-	-	-	-	-
Th	Free	48.7	46.0	43.1	40.6	37.4	34.1
	with SO ₄	51.3	54.0	56.9	59.6	62.6	65.9
	Free	4.4	3.7	3.1	2.8	2.5	2.2
	with SO ₄	95.6	96.3	96.9	97.2	97.5	97.8
Ionic Strength		1.23	1.06	0.94	0.86	0.81	0.78

* pFe = -0.68 and pSO₄ = -0.98

TABLE A.7: SATURATION INDEX FOR JAROSITE IN DIFFERENT WATERS

Water	Description*	pFe _T	pFe ³⁺	pK _T	pK ⁺	PSO ₄ T	PSO ₄ ²⁻	I (m)	SI*	Any Fe(OH) ₃ (s)
1	L1 (low) before decline	.0186	0.60	2.07	2.07	0.107	2.1	1.36	2	No
2	L1 (low end operation)	1.05	2.3	-3.9	3.9	0.885	1.8	0.074	4	No
3	L7 (low) before decline	0.114	1.0	2.3	2.3	0.025	1.4	0.637	5	No
4	L7 (low) middle of decline	0.314	1.3	2.6	2.6	0.198	1.4	0.353	8	No
5	L7 (low) end of operation	1.05	2.5	4.3	4.3	0.745	1.4	0.110	0.8	No
6	L2 (high) before decline	2.38	3.7	4.1	4.1	2.19	2.5	0.0105	30	pFe _s =3.2; 15% of Fe _T
7	L2 (high), middle of decline	3.43	4.8	4.1	4.1	2.55	2.6	.00652	0.002	No
8	L2 (high) end of operation	4.33	6.7	3.9	3.9	3.23	3.3	0.0017	0.006	pFe _s =4.6; 56% of Fe _T
9	L8 (high) before decline	2.49	4.1	4.0	4.0	2.26	2.4	0.0108	4	pFe _s =2.8; 44% of Fe _T
10	L8 (high) end of operation	4.35	6.5	4.3	4.3	2.97	3.0	0.00268	0.0005	No

$$SI^* = \frac{[K] [Fe^{3+}]^3 [SO_4]^{-2} [H^+]^{-6}}{10^{-9.4}}$$

* bracket (low) describes rate of water application to lysimeter; before, middle of decline, end of operation refers to start, middle or end of decline of TDS during last 1.5 years of lysimeter operation.

TABLE A.8:

RATIOS OF SEVERAL MAJOR ELEMENTS DERIVED FROM
PROTON ATTACK UPON ALUMINO SILICATES

(a) F, Ca, Mg, and K:Al; K:Mg

Lysimeter	Molar Ratios of Elements on Leachate			
	F/Al	Ca/Al	Mg/Al	K/Al
Low Rate (L1, L7)	0.024±0.01 (n=8)	0.1±0.13 (n=11)	0.033±0.005 (n=11)	7 0.23±0.04 (n=10)
Low Rate (L7 by itself)	-	0.039±0.015 (n=7)	-	-
High Rate (L2, L8)	-	0.33±0.2 (n=12)	0.078±0.036 (n=12)	15 1.5±0.89 (n=12)

(b) Silica: Aluminum

Sample	Water	Lysimeters	Description of Time of Sampling	Si/Al Molar Ratio
29	-	L1	Near start of decline of TDS for low-rate	0.11
32	3	L2	Beginning of decline of TDS for low-rate	0.11
38	5	L2	End of lysimeter operation for low-rate	3.8
50	10	L8	End of lysimeter operation for high-rate	18

(c) Ratio of Major Elements in Various Minerals

	F/Al	Co/Al	Mg/Al	K/Al	K/Mg	Si/Al	Comments
1. Typical Character.							
of Nordic Lake Area							
Tailings							
(Zahary et al, 1974)							
(a) Coarse Tailings	-	0.094	0.022	0.39	1.7	20	
(b) Fine Tailings	-	0.268	0.022	0.36	17	16	
2. Representative Minerals							
Plagioclase (andesine)							
($\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$)	0	0.33	0	0	-	1.7	Not probable:
Congruent Dissolution	-	∞	-	-	-	∞	Na is too high
Incongruent Dissolution							
Kfeldspar (orthoclase)							
(KAlSi_3O_8)	0	0	0	1	-	3	
Congruent Dissolution	-	-	-	00	-		
Incongruent Dissolution							
Biotite							
($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$)	0	0	3	1	0.33	3	
Congruent Dissolution	-	-	∞	∞	-	∞	
Incongruent Dissolution							
Quartz (SiO_2)	0	0	0	0	-	0	Si(O) ₄ is dis-
Congruent Dissolution	-	-	-	-	-	-	solution product

TABLE A.9: SILICA CONCENTRATIONS IN 4 SAMPLES

Sample	Water	H ₄ SiO ₄ (as Si, mg/L)	SI
28	-	61.1	1.1
32	3	61.1	1.1
38	5	79.8	1.4
50	10	20.6	0.4

SI = $p\text{Si}/pK_{\text{SiO}_2}$; $pK_{\text{SiO}_2} = 2.7$ for amorphous SiO₂

TABLE A.10: METABOLISM OF LYSIMETERS OF EXPERIMENT I

Molar Ratios	Low Rate Lysimeters (L1, L7)	High Rate Lysimeters (L2, L8)
C/N	27 ± 13 (n=10)	14 ± 11 (n=9)
<u>with respect to S</u>		
NH ₃ -N/S	0.51 ± 0.36 (n=10)	12 ± 8 (n=10)
C/S	2.7 ± 0.71 (n=10)	50 ± 76 (n=10)
<u>with respect to Fe</u>		
NH ₃ -N/Fe (mM N/M Fe)	0.71 ± 0.47 (n=10)	28 ± 19 (n=10)
TOC/Fe (mM C/M Fe)	14.3 ± 3.6 (n=11)	170 ± 69 (n=8)

TABLE A.11:
PHYSICAL DESCRIPTION OF LYSIMETERS

Lysimeter L₁ (low rate; 3 in ID core)

1. General - The entire core is a uniform, pale buff colour. There is no horizontal stratification observable. The total core length is 85 cm.
2. Particular Comments (depth given as from top)
 - (a) Section 4: (30-40 cm) a pyritic bleb found
 - (b) Section 6-9 (50-82 cm) - occasional pyritic lenses
 - one pyritic bleb of ca 0.5 cm diameter is found at 69 cm
 - (c) Sections 8-9 (70-82 cm) is a little darker than upper material. This may be due to higher moisture or the pyrite lens.
 - (d) Section 8 (70-80 cm) has ca 1 cm lens of rounded quartz sand
 - (e) Section 9 (80-85 cm) in the top 2 cm are tailings; in the bottom 3 cm (82-85 cm) are silica sand assumed to be the bedding inserted into the lysimeter before addition of tailings
 - (f) Section 9 (82 cm) A thin, 0.2 cm thick orange oxide band is found at the top of the sand.

Lysimeter 2 (High Rate; 3 in ID Core)

1. General. The total core length is 85 cm.
2. Particular Comments
 - (a) Section 1 (0-5 cm), is uniform orange with rare pyritic blebs. There are pyrite nodules at ca 1 cm depth with coatings.
 - (b) Section 1-2 (5-10.5 cm) is a mottled orange colour with decreasing orange colour with depth.
 - (c) Section 2 (10.5-12 cm) is the zone of fairly rapid transition from the orange colour to the uniform buff colour with occasional orange mottles (i.e. oranges covers < 5% of surface).
 - (d) Section 2-6 (12-52 cm) is uniform buff colour; the orange mottles are occasional to rare.
 - (e) Section 6-8 (52-76.5 cm) is uniform buff colour with rare orange mottling.

Table A.11 cont'd

- (f) Section 8 (at 76.5 cm). There is a ca 0.3 cm thick band of orange "oxides" separating the "oxidized" buff coloured tailings from the reduced tailings below.
- (g) Section 8-9 (76.8-82) is a blotchy, medium gray colour with prominent pyrite-rich patches.
- (h) Section 9 (82-85 cm) contains silica sand placed before addition of tailings.

Lysimeter L7 (low rate; 3 in ID core)

1. General

2. Particular Comments

- (a) Orange-brown mottled appearance on outer surface of core when tube was moved. This is more prominent below 40 cm. It is very dark at 70-80 cm.
- (b) Section 4 (37 cm) has a dark cluster of pyrite grains, showing this to be the oxidation zone.
- (c) Section 4 (30-40 cm) - Pyrite clusters are evident in this section, but not in above sections. The pyrite tends to occur in clusters of ca 2-4 mm diameter.
- (d) Section 5 (40-50 cm)-Prominent pyrite lens (3mm thick) and mottled pyritic zones (2-4 mm thick) are observed, but no oxidized appearance.
- (e) Section 6 (50-60 cm) has a prominent mottled grey appearance due to pyritic grain clusters.
- (f) Section 7 (60-70 cm)-Pyritic lenses are found up to 12 mm across and 15 to 20 mm long. The areas, shaped  indicate substantial heterogeneity.
- (g) Section 8-9. At 78 cm, there is a sharp colour boundary. Below this boundary (between 78-84 cm), it is a dark grey, pyritic layer. This zone is heavily mottled with orange-brown colour only on the outer rim of the core.
- (h) Section 5. The major boundary between unmottled (above) and mottled orange-brown on the outer surface of the cores material is at 48 cm.

Lysimeter L8 (High Rate; 3 in ID core)

General. The core is a pale yellow, but orange colour is prominent.

Particular Comments

- (a) Section 1 (0-10 cm). The top 8 cm is fairly dried out, the deep orange brown colour penetrates through the core but inner zones of grey pyrite are viable in clusters of 2-4 mm diameter. There is a 5 mm thick x 30 mm wide rose coloured band at 3 cm depth.
- (b) Section 1 (at 10 cm). There is a discontinuous boundary of 10 cm blending from the deep orange to mottled-orange yellow to yellow colour below.
- (c) Section 2-3 (10-24 cm). Prominent horizontal bands, 10 mm thick, appear intercollating with the yellow, to a depth of 24 cm.
- (d) Section 5. At 55 cm, the orange mottling colour disappears; below, a pale yellow colour is observed almost exclusively.
- (e) Section 8. At 70-80 cm, a wavy but distinct boundary occurs between the pale yellow above and the medium to dark grey pyritic colour below.
- (f) Section 9. The tailings layer from 80 to 86 cm is the dark grey pyritic colour. The bottom 3 cm (86 to 89 cm) contains silica sand. A thin abrupt zone of pale orange coloration is observed at the top of the silica sand (86 cm).

TABLE A.12: COMPOSITION OF LYSIMETER SOLIDS

Section	Depth	Ra-226 pCi/gm	Th-230 pCi/gm	Th-232 pCi/gm	Sulfide (%)	Sulfate as Gypsum (%)	Carbonate (%)	Porosity	Moisture % of Tot. Vol.	Bulk Density gm/cc
a) Lysimeter No. 1, (Low Rate)										
1					0.07	0.09	*	-	-	1.23
2					-	-	*	0.55	0.04	1.32
3					0.07	0.09	*	0.52	0.05	1.29
4					-	-	*	0.53	0.05	1.38
5					0.09	0.15	*	0.50	0.05	1.31
6					-	-	*	0.52	0.06	1.36
7					0.54	0.16	*	0.51	0.07	1.33
8					0.19	0.20	*	0.52	0.07	1.38
9					0.81	0.21	*	0.50	0.1	
* Assumed as 0.001 based upon L7 and L8 results Avg $P_B = 1.32 \pm 0.05$ g/cm ³										
b) Lysimeter No. 2 (High Rate)										
1					0.11	0.036	*	-	-	1.27
2					-	-	*	0.54	0.05	1.31
3					0.05	0.011	*	0.52	0.06	1.32
4					-	-	*	0.52	0.07	1.26
5					0.06	0.014	*	0.54	0.08	1.30
6					-	-	*	0.53	0.09	1.33
7					0.05	0.005	*	0.51	0.12	1.30
8					1.11	0.018	*	0.53	0.16	1.40
9					2.94	0.036	*	0.49	0.22	

* Assumed as <0.001% based upon L7 and L8 results
Avg. $P_B = 1.31 \pm 0.04$ g/cm³

TABLE A.12 (cont'd) COMPOSITION OF LYSIMETER SOLIDS

Section	Depth	Ra-226 pCi/gm	Th-230 pCi/gm	Th-232 pCi/gm	Th-228 pCi/gm	Sulfide (%)	Sulfate as Gypsum (%)	Carbonate (%)	Porosity	Moisture % of Tot. Vol.	Bulk Density gm/cc
c) Lysimeter No. 7 (Low Rate)											
1		150	15.4	2.7	5.1	.09	0.08	.001	.54	0.04	1.4
2						-	0.007	-	.52	0.05	1.27
3		140	24.2	3.5	7.6	.05	0.03	.001	.53	0.05	1.25
4						.04	0.013	-	.52	0.05	1.27
5		110	9.4	1.7	2.8	.34	0.01	.001	.53	0.06	1.24
6						.56	0.023	-	.51	0.07	1.27
7		120	9.4/11.3	2.0/1.8	3.0/3.7	1.09	0.1	.001	.50	0.13	1.33
8						0.65	0.27	-	.49	0.14	1.34
9		70	14.5	2.1	3.3	2.77	1.21	.001	.42	0.35	1.53
For Lysimeter 7, $P_B = 1.30 + 0.1 \text{ g/cm}^3$											
d) Lysimeter No. 8 (High Rate)											
1		30	17/13.6	4.1/2.1	1.0/2.5	0.66	0.01	.001	.51	0.04	1.30
2						0.06	0.009	-	.51	0.04	1.31
3		180	18.7/14.8	3.5/2.0	6.3/4.7	0.06	0.005	.001	.52	0.04	1.26
4						0.06	0.005	-	.53	0.05	1.24
5		150	16.1	2.4	4.7	0.06	0.05	.001	.52	0.07	1.28
6						0.06	0.01	-	.52	0.07	1.26
7		120	16.6	3.3	5.4	0.07	0.006	.001	.51	0.09	1.29
8						0.39	0.11	-	.50	0.12	1.33
9		130	12.0	2.2	4.2	0.40	0.53	.001	.46	0.19	1.43
For Lysimeter 8, $P_B = 1.30 + 0.06 \text{ g/cm}^3$											

TABLE A.12 (cont'd)

COMPOSITION OF LYSIMETER SOLIDS

e) Mill Samples							
Sample	Ra-226 pCi/gm	Th-230 pCi/gm	Th-232 pCi/gm	Th-228 pCi/gm	Sulfate Sulfide (%)	as Gypsum (%)	Carbonate (%)
Leaching Pachucas	230	30	180	40	1.17		0.001
Partial Neut	310	50	250	50	1.58	4.1	0.045
Final Neut	300	80	480	90	1.74	4.3	0.020

TABLE A.13a: LEACHING CHARACTERISTICS OF RADIOISOTOPES FROM SOLIDS

	Typical Initial Mass from Mill ⁺	Mass Initial Lysimeter	Amount Leached	% Leached
--	--	------------------------------	-------------------	--------------

Low Rate

Th-230	29	1.38	.0839	6
Ra-226	29*	10.6	.0024	0.02%
Th-232	7.7	.234	.0139	6
Th-228	7.7	.433	.0328	8

High Rate

Th-230	29	1.55	.147	9.5
Ra-226	29	11.1	.0845	0.8%
Th-232	7.7	0.3	.0188	6
Th-228	7.7	0.56	0.17	30%

* Calculations based upon typical tailings composition and 90 kg of tailings.

* If coarse tailings are used as model, typical mass would be 16.6 x .09
= 1.5 u Ci per lysimeter

A.13.b AVERAGE CONCENTRATIONS OF RADIOISOTOPES IN LYSIMETER SOLIDS

	<u>Low Rate</u>	<u>High Rate</u>
Ra-226 (pCi/g)	118	122
Th-230 (pCi/g)	15	16
Th-232 (pCi/g)	2.4	3.1
Th-228 (pCi/g)	4.4	4.3

Table B.1 CHARACTERISTICS OF FILTERS USED TO REMOVE PRECIPITATES FORMED AFTER SULPHATE LEACH

		L1 - 2 - 9 Heavy Orange	L2 - 2 - 9 v. light orange	
		L1 - 2 - 8 Light orange	L2 - 2 - 8 Clear	
L7 - 1 - 8 Heavy orange	L8 - 1 - 8 Heavy orange	L1 - 2 - 7 Heavy orange	L2 - 2 - 7 v. light buff	
L7 - 1 - 6 Heavy orange	L8 - 1 - 6 Clear	L1 - 2 - 5 Heavy orange	L2 - 2 - 5 Clear	FT v. light orange to buff
L7 - 1 - 4 light yellow buff	L8 - 1 - 4 Missing	L1 - 2 - 3 Moderate orange	L2 - 2 - 3 Clear	PH v. light orange
L7 - 1 - 2 Clear	L8 - 1 - 2 v. light buff	L1 - 2 - 1 Moderate orange	L2 - 2 - 1 v. light buff to orange	LP (To #12) v. light buff

TOTAL: 23 FILTERS

Table B.2

Sample	Isomer Shift (mm s^{-1})*	Quadrupole Splitting (mm s^{-1})
Leaching Discharge	0.338 ± 0.009	0.600 ± 0.008
L8-1-1	0.35 ± 0.01	0.62 ± 0.01
L7-1-8	0.34 ± 0.02	0.626 ± 0.0
L7-1-10	0.35 ± 0.03	0.65 ± 0.03
FeS ₂	0.31	0.61
Jarosite	0.43	1.20

* Relative to natural iron.



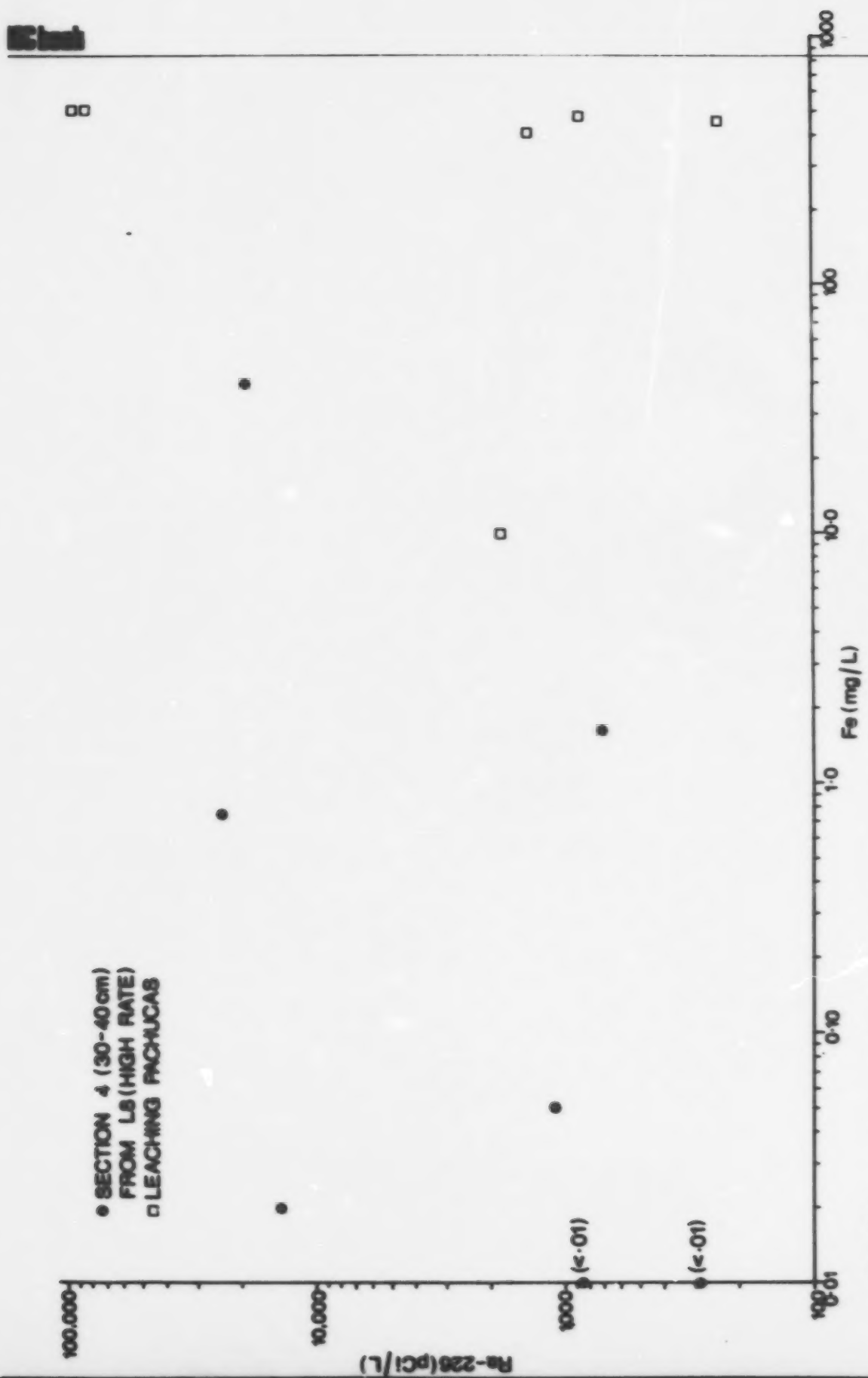


Fig. 4.5.1. Scattergram from Washing Experiment of Ra-226 versus Iron

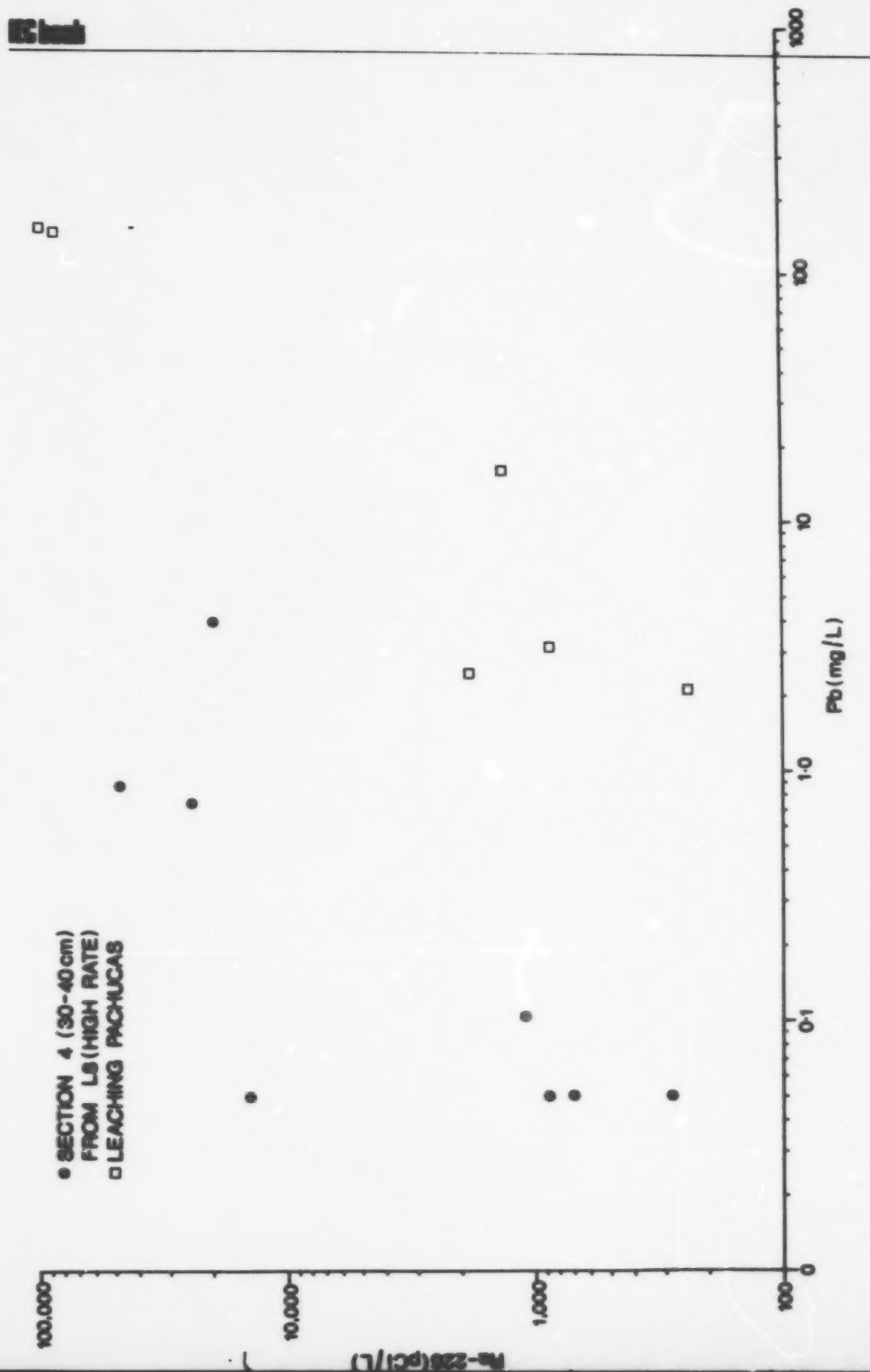


Fig. 4.5.2. Scattergram from Washing Experiment of Ra-226 versus Lead

FIG. 4.5.3 Scattergram from washing experiment of Ra-226 versus Calcium

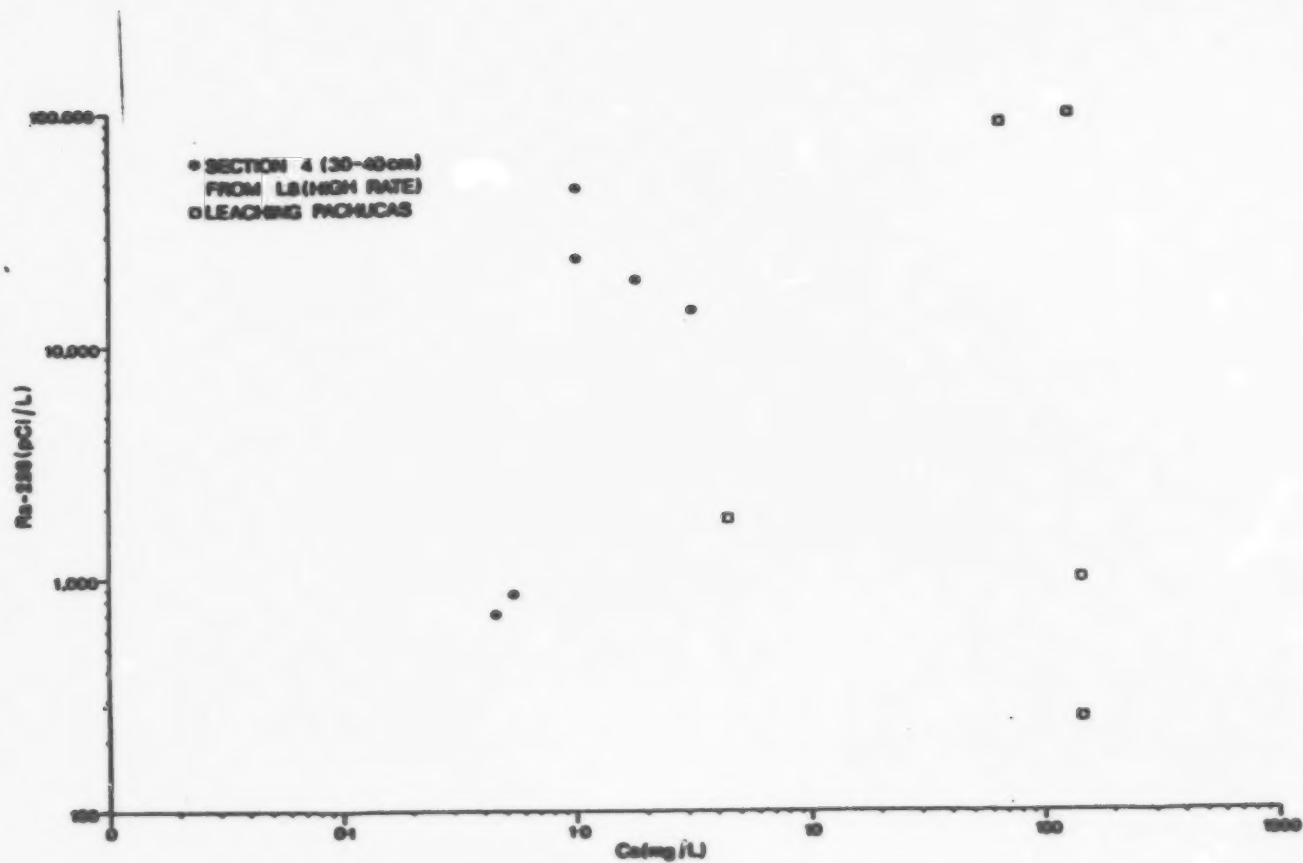


FIG. 4.5.4 Scattergram from washing experiment of Ra-226 versus Barium

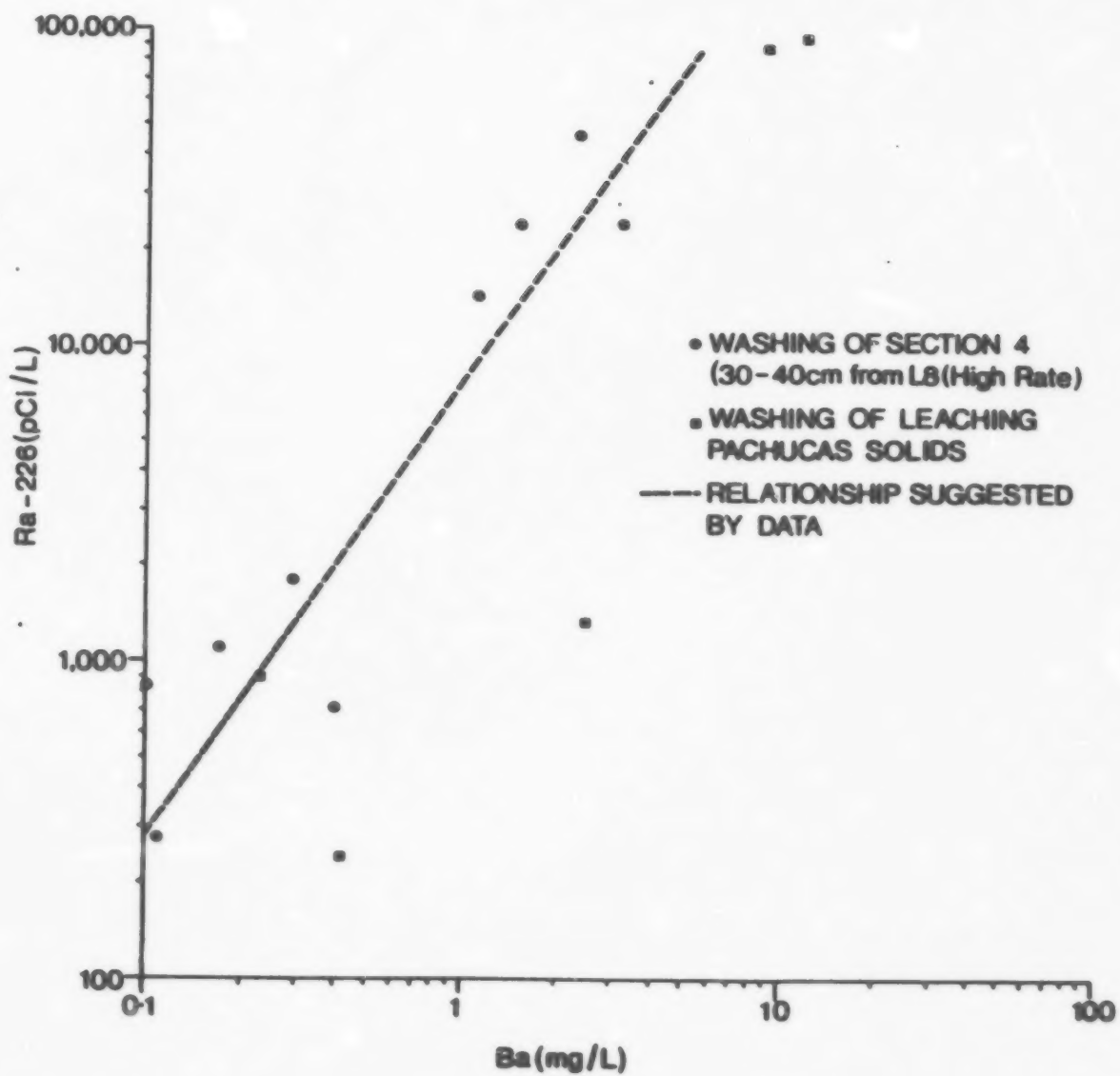


FIG. 58a Plot of Ratio of Mass Ra-226 (nCt) to mass of TDS (mMol) leached to TDS concentration (mMol/L) for Madawaska Tailings (Experiment 4)

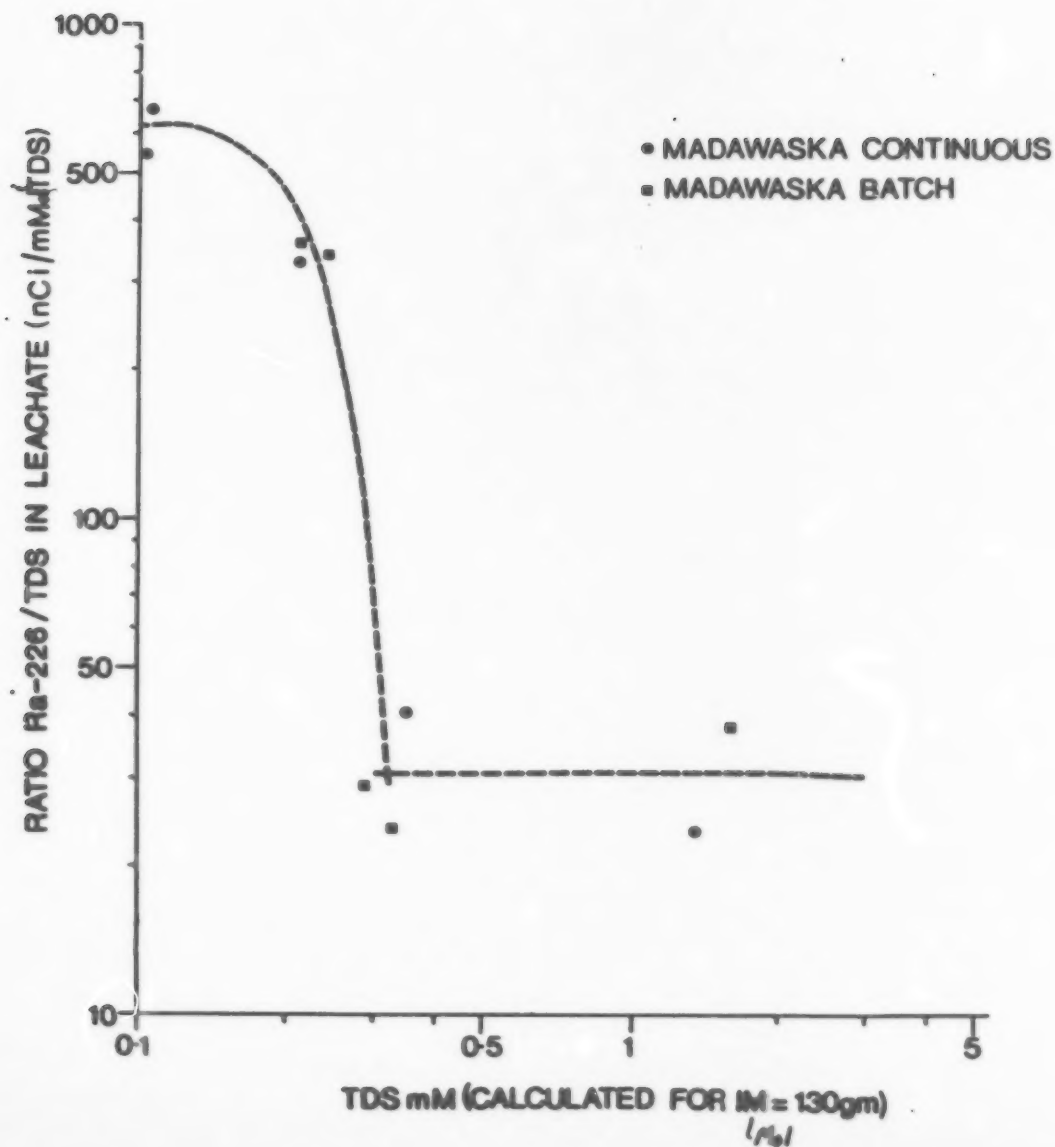


FIG 58b Plot of Ratio of Mass of Ra-226 leached (nCi) to Mass of sulfate (mMol) leached with sulfate concentration (mMol) for Madavaska Tailings (Experiment 4)

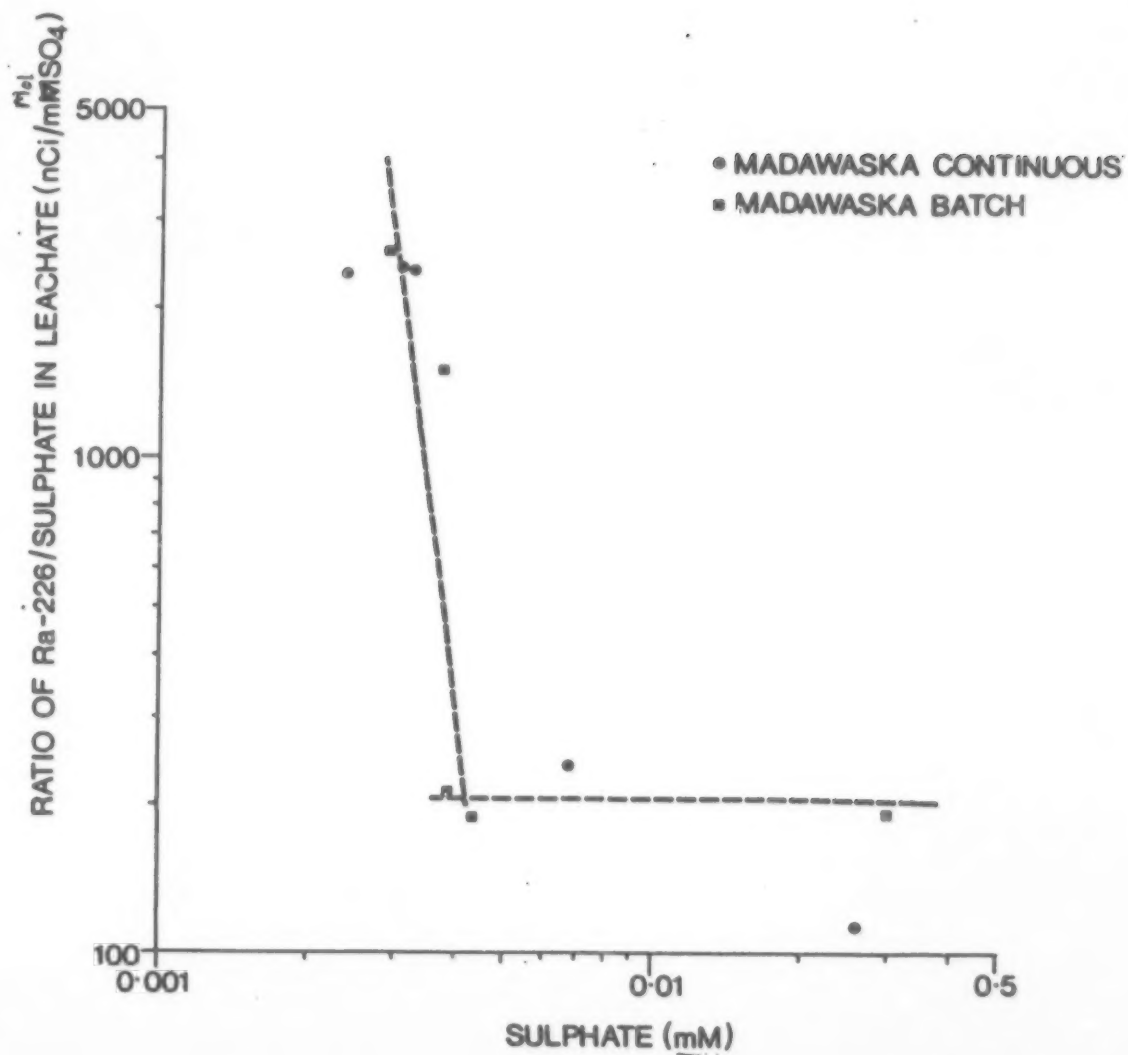


FIG 58c Plot of Ratio of mass of Ra-226 leached (nCi) to mass of TDS leached (Mol) with TDS concentration (mMol/L) for Rio Algom Tailings (Experiment 4)

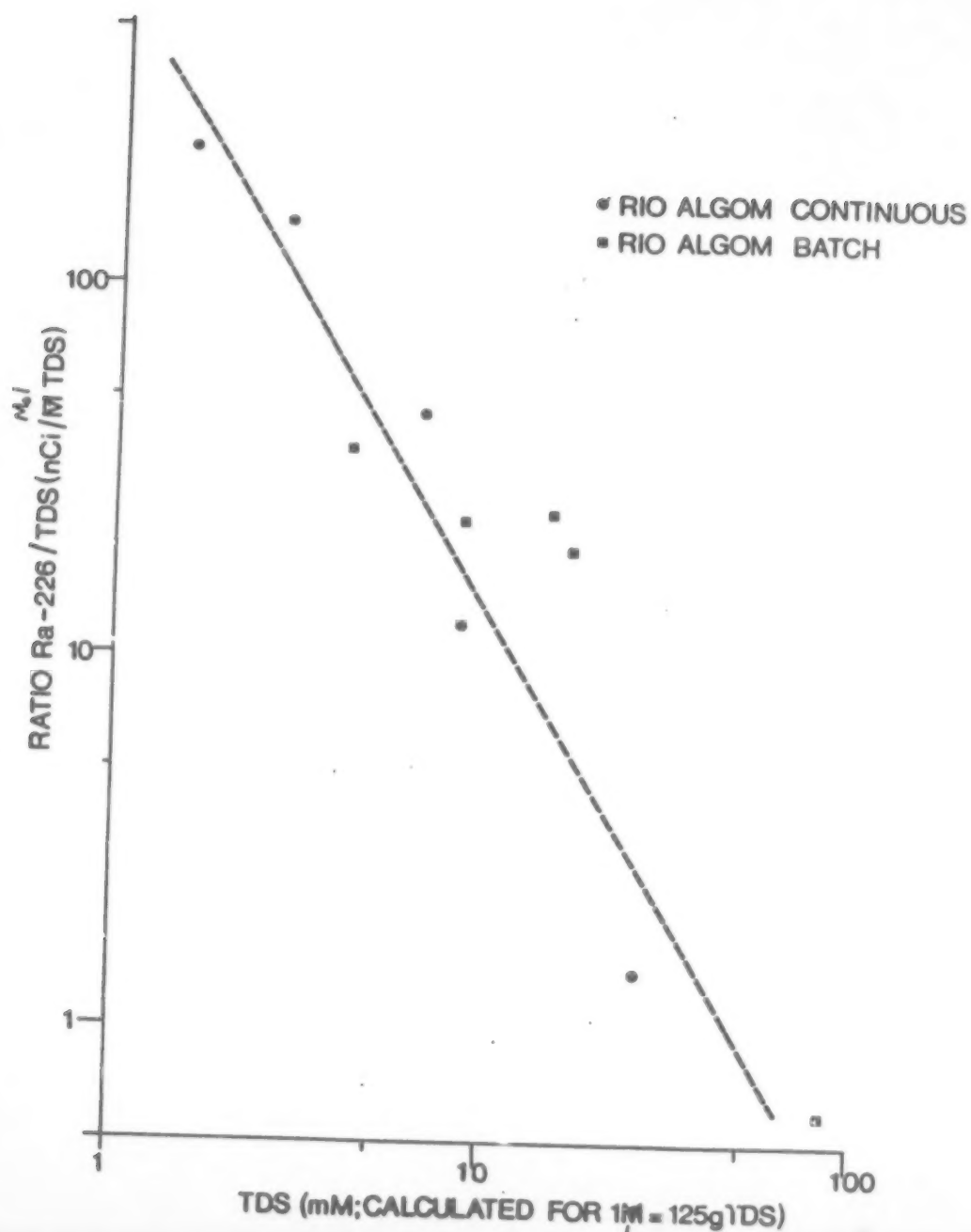


FIG. 58d Plot of Ratio of Mass of Ra-226 leached (nCi) to mass of sulfate leached (Mol) with sulfate concentration (mM) for Rio Algom tailings (Experiment 4)

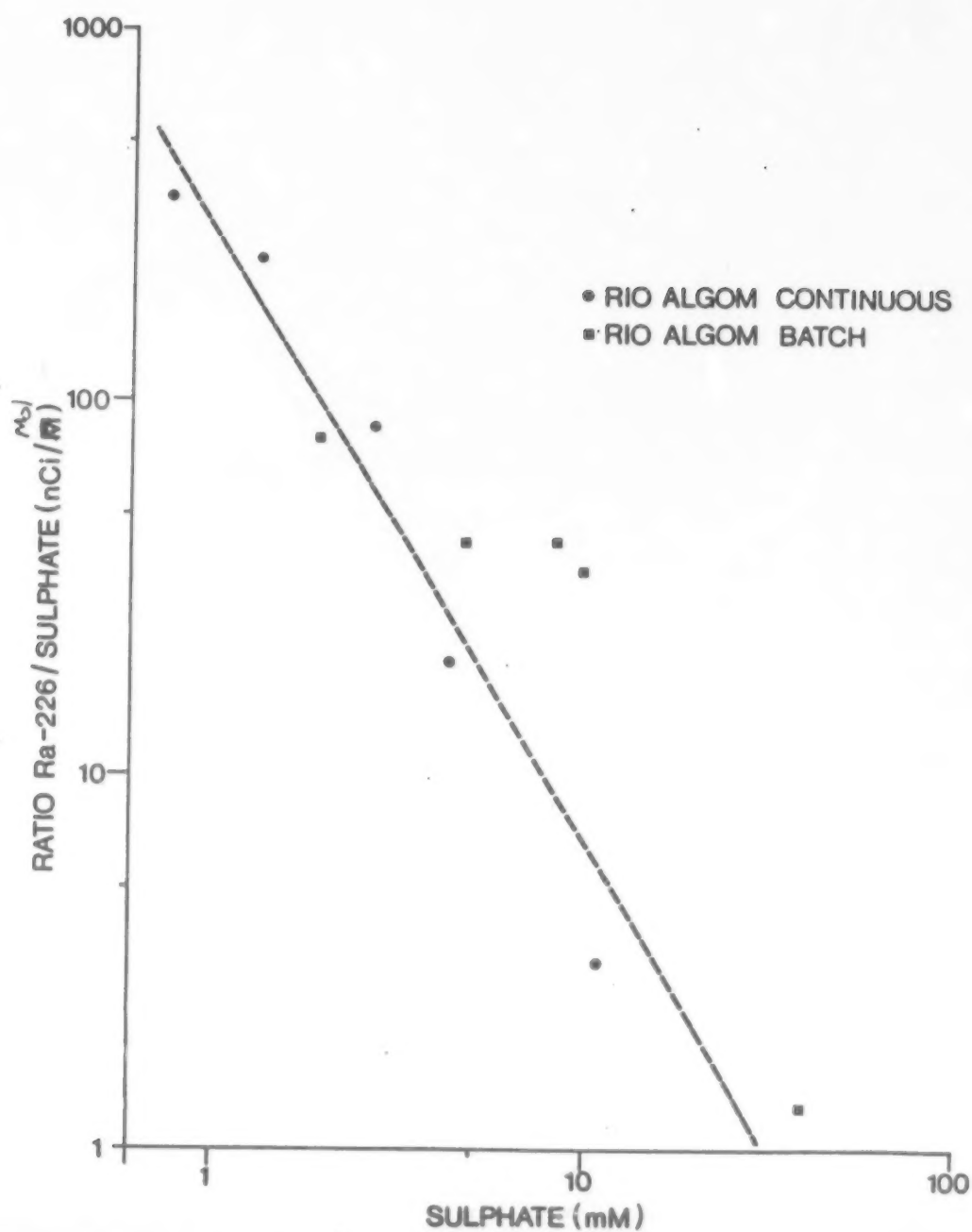


FIG. 9.1

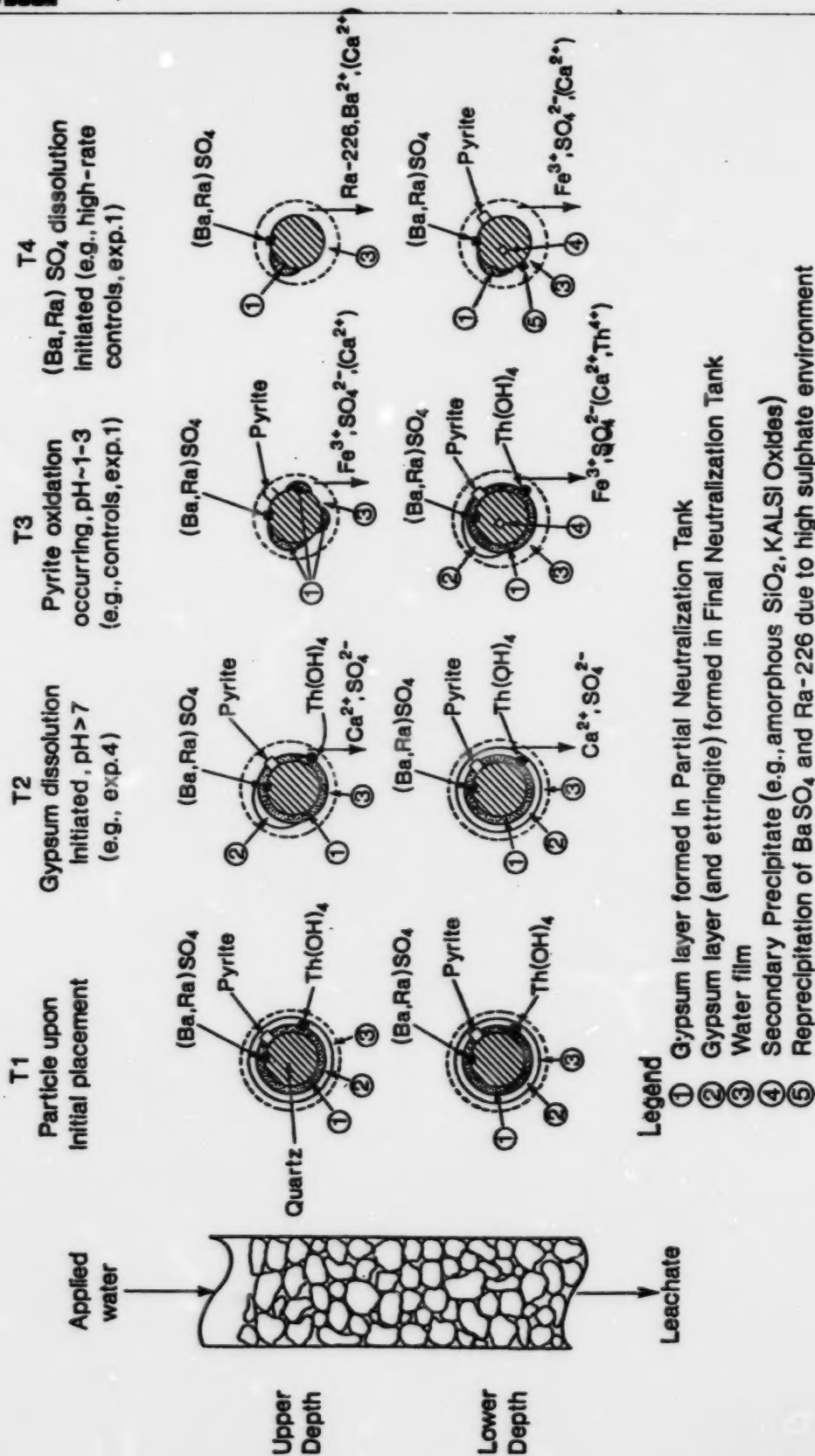


FIG. A.1 Comparison of Measured TDS with calculated TDS

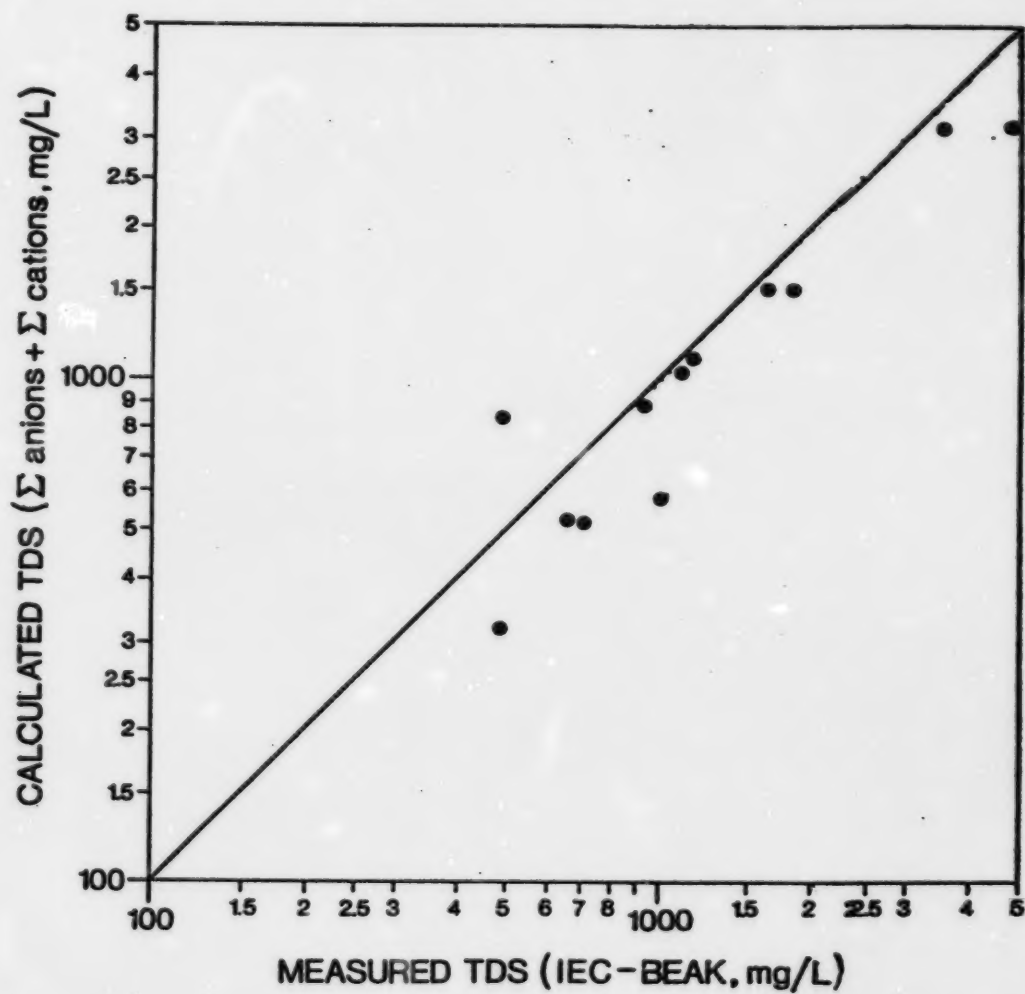


FIG. A.2 Comparison of measured TDS with calculated TDS for leachate from high rate lysimeter when nitric acid concentration is removed from estimates for TDS

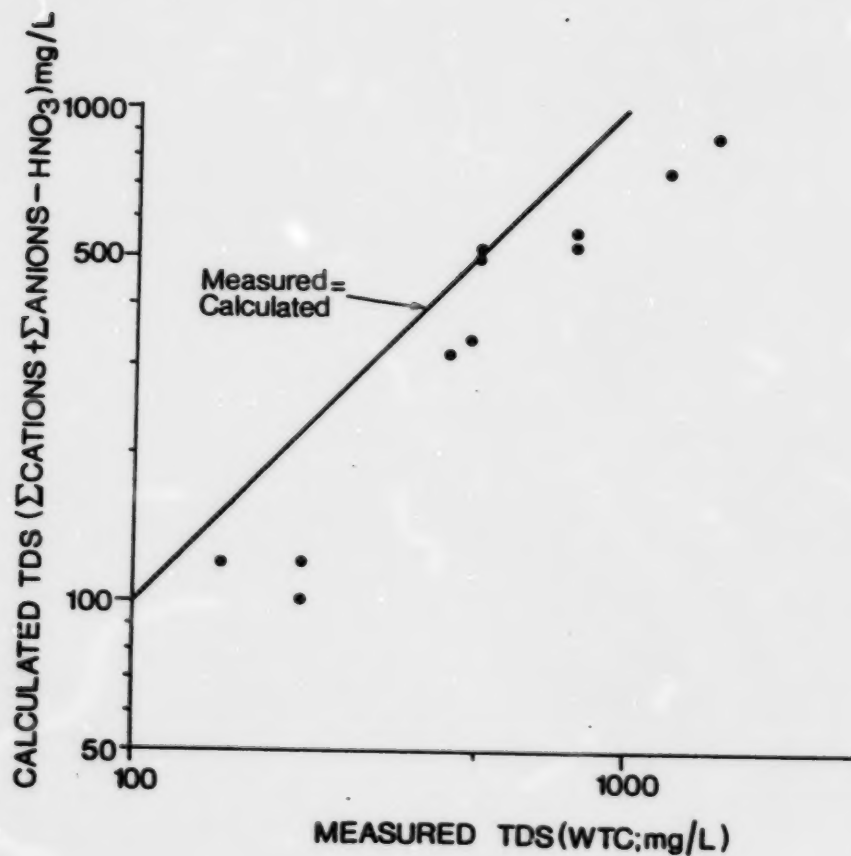


FIG. A.3 Comparison of Measured TDS and calculated TDS for leachate from low rate lysimeter

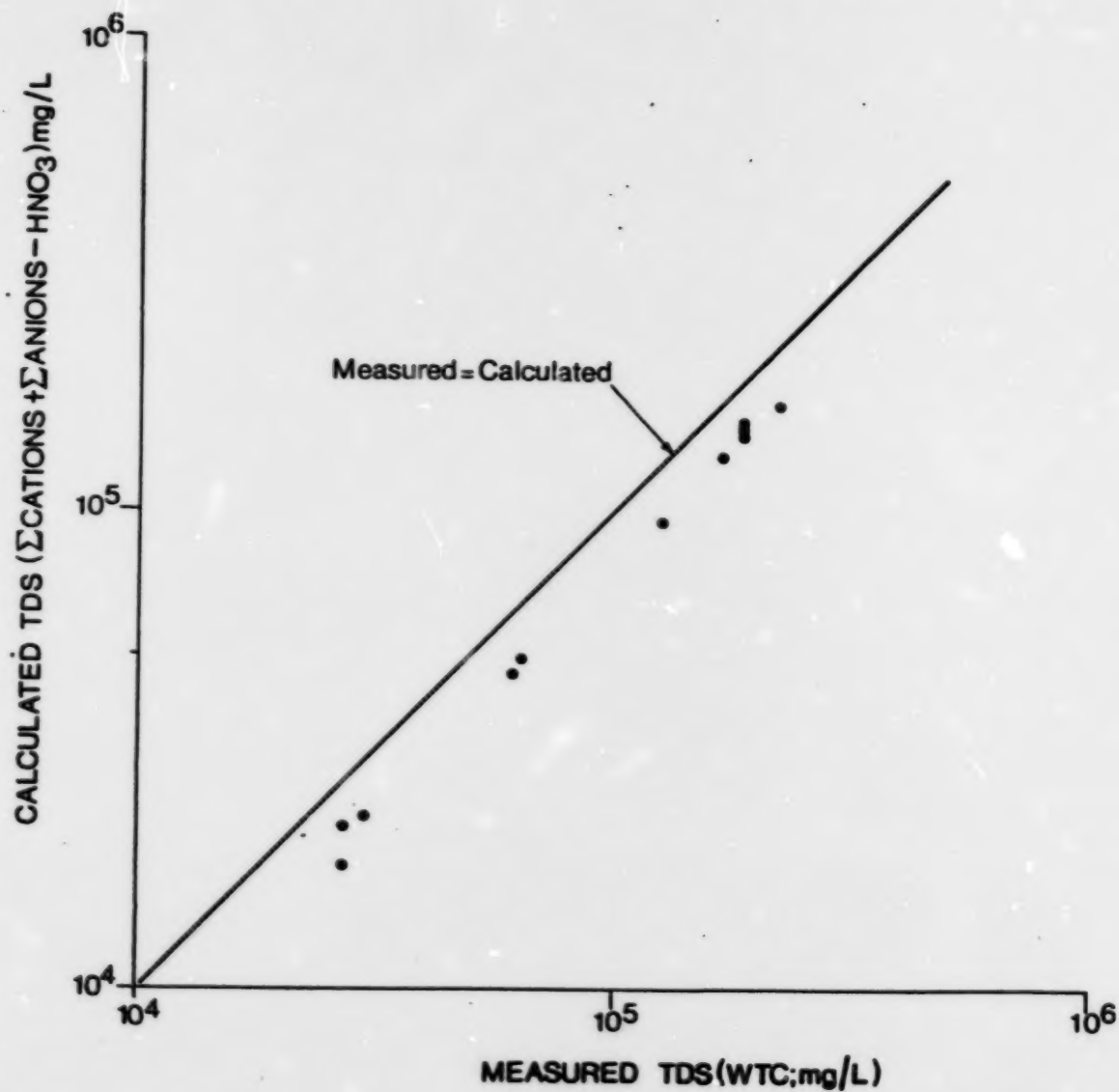


FIG. A.4 Comparison of TDS Measured by WTC and IB for low rate lysimeter

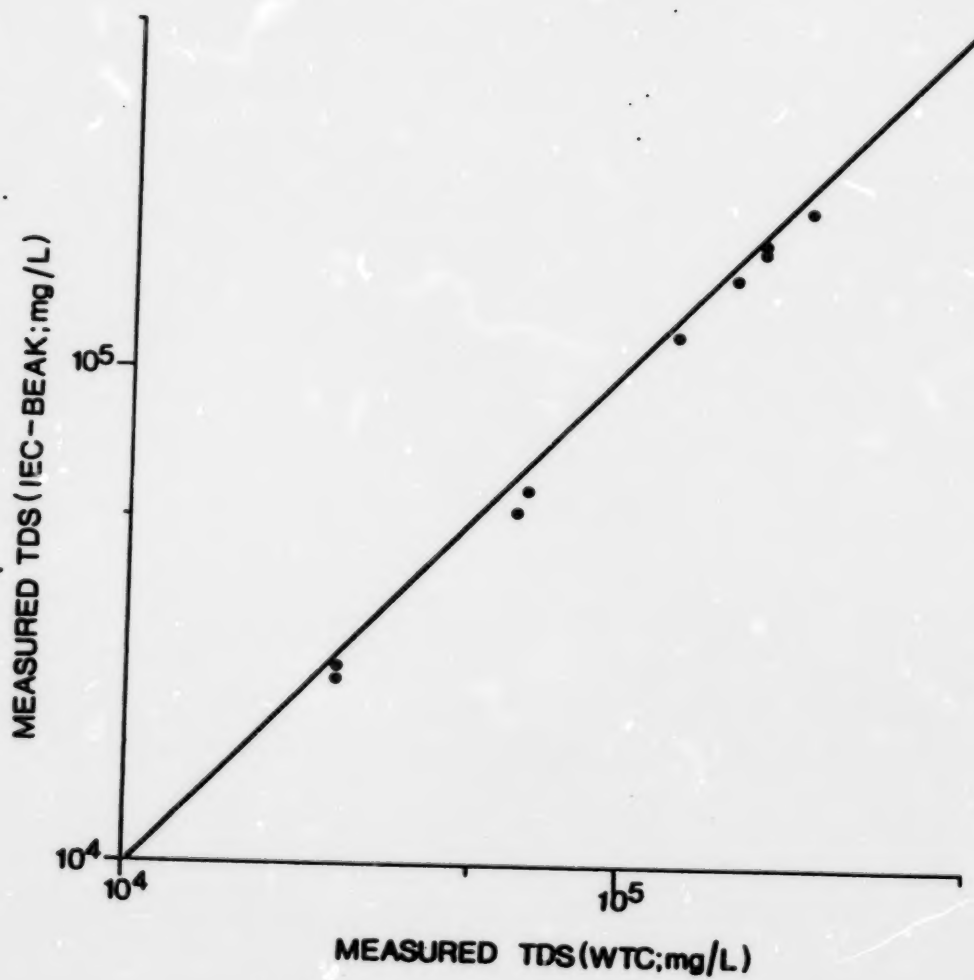


FIG. A.5 Comparison of sulfate plus nitrate with measured acidity for leachate from high rate lysimeter

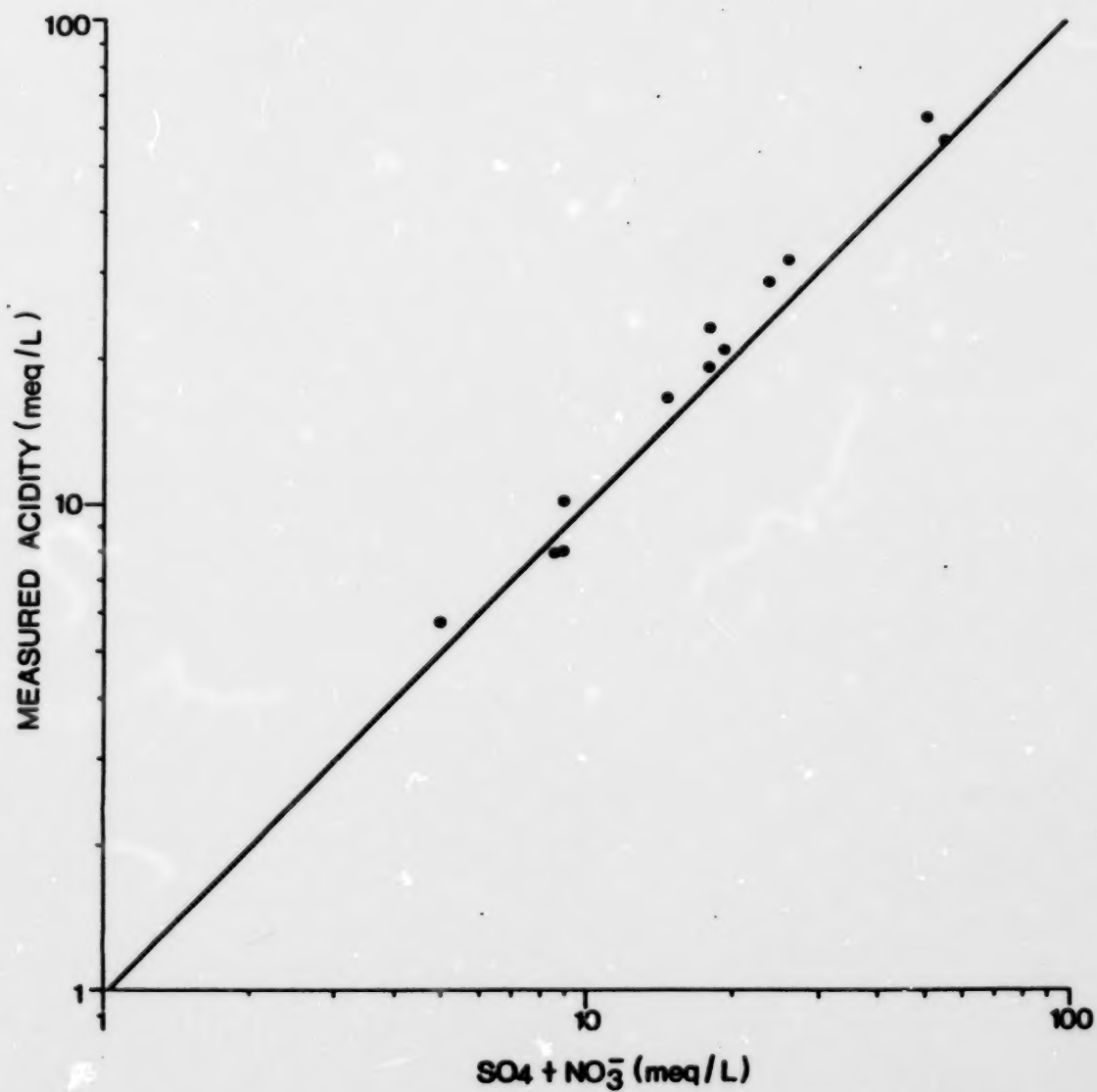


FIG. A.6 Comparison of sulfate and measured acidity without HNO_3 for leachate from high rate lysimeter

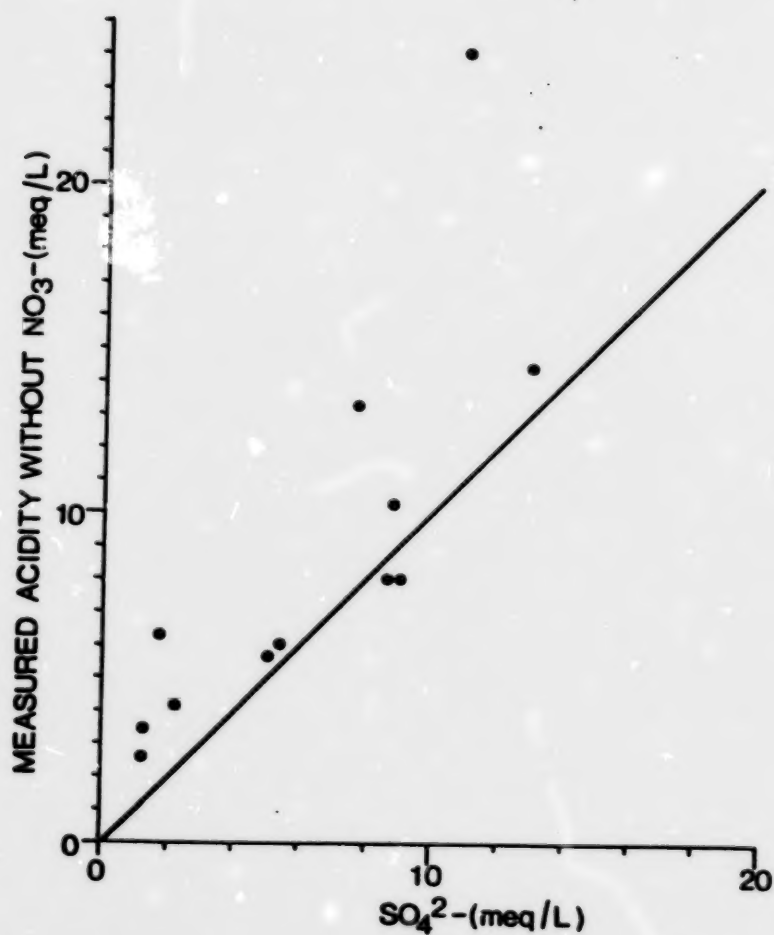


FIG. A.7 Comparison of sulfate and measured acidity for leachate from high rate lysimeter

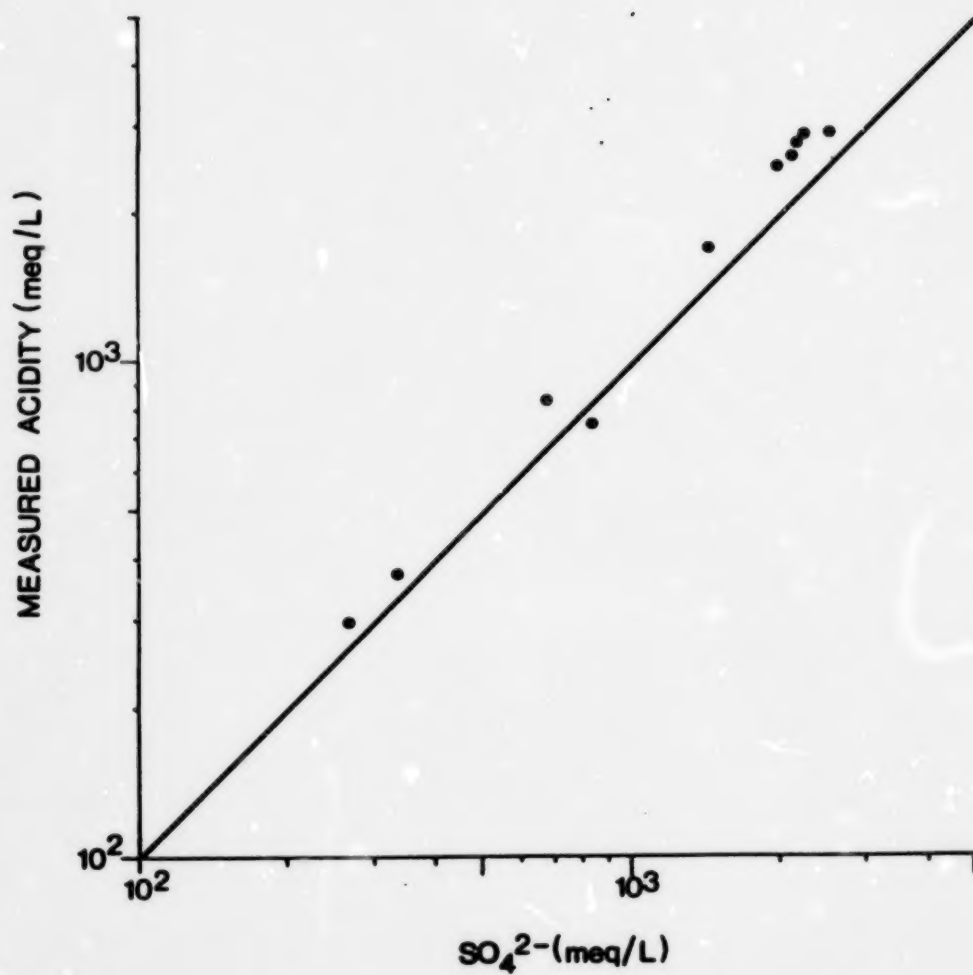


FIG. A.8 Comparison of Conductivity and TDS for leachate from all lysimeters (circled points had nitric acid added)

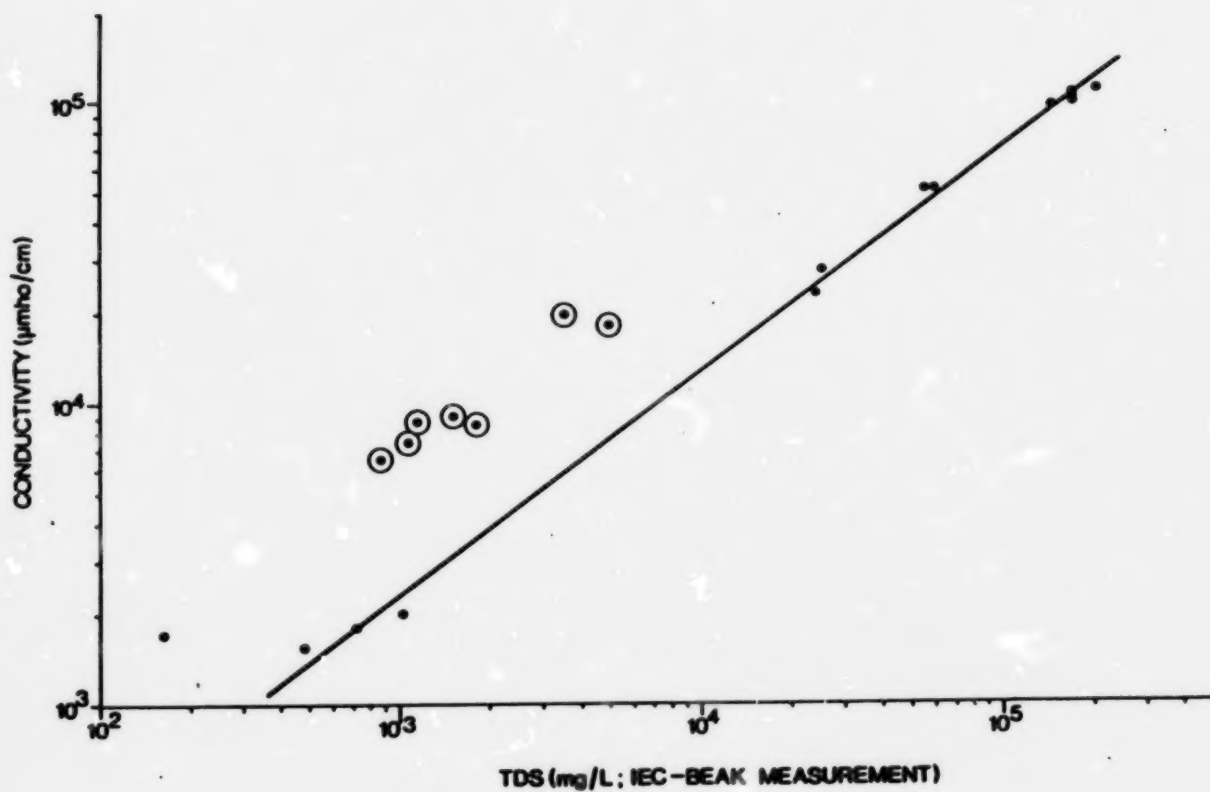


FIG. A.9 Bjerrum Diagram for Water 1 (Actual pH = 0.7)

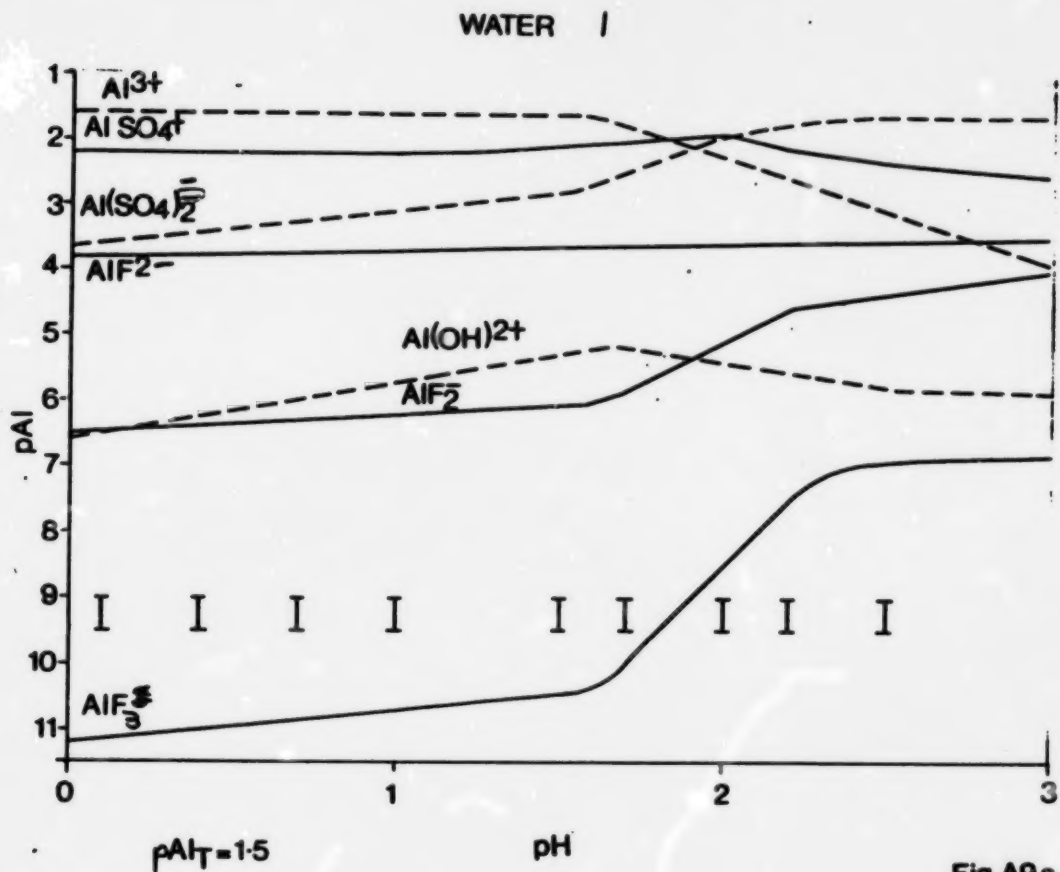


Fig.A9a.

Al

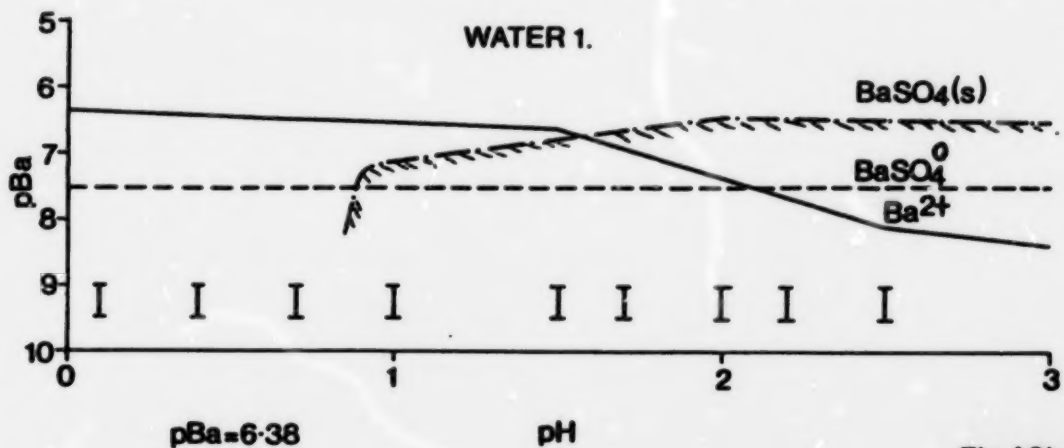
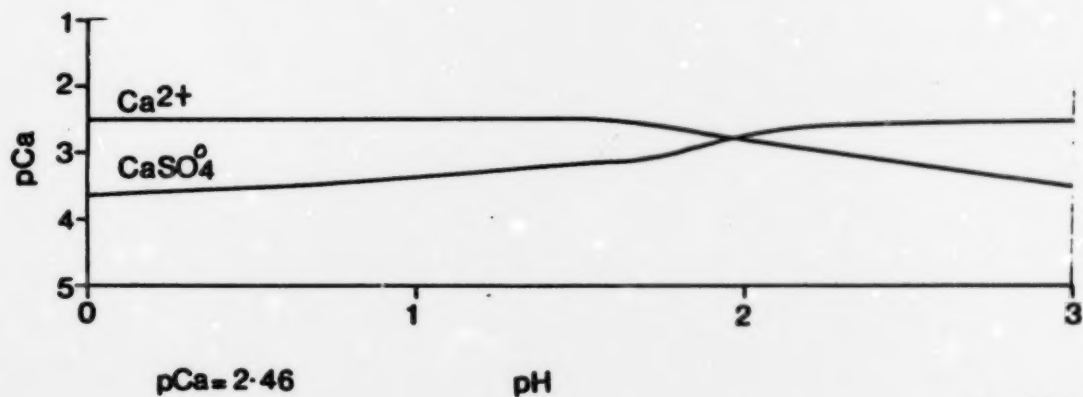
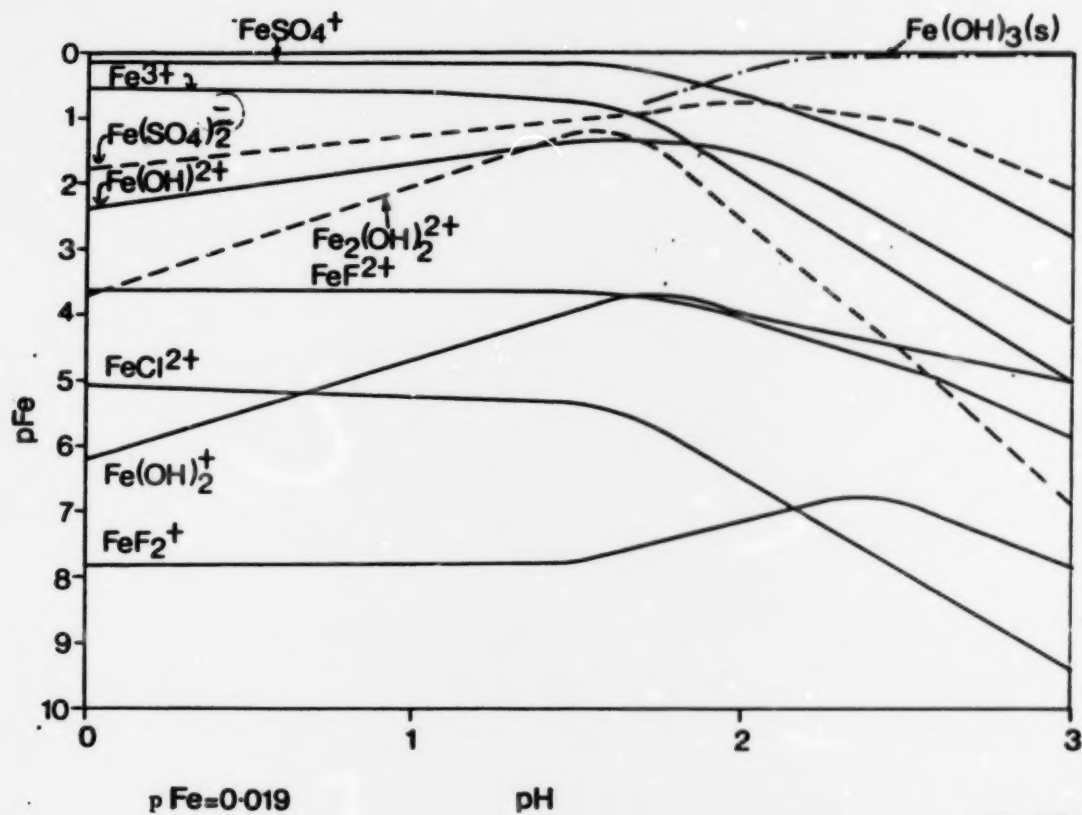


Fig.A9b.

Ba

I = POINT OF EVALUATION

FIG. A.9 (cont'd) Bjerrum Diagram for Water 1



EC book

FIG. A.9 (cont'd) Bjerrum Diagram for Water 1

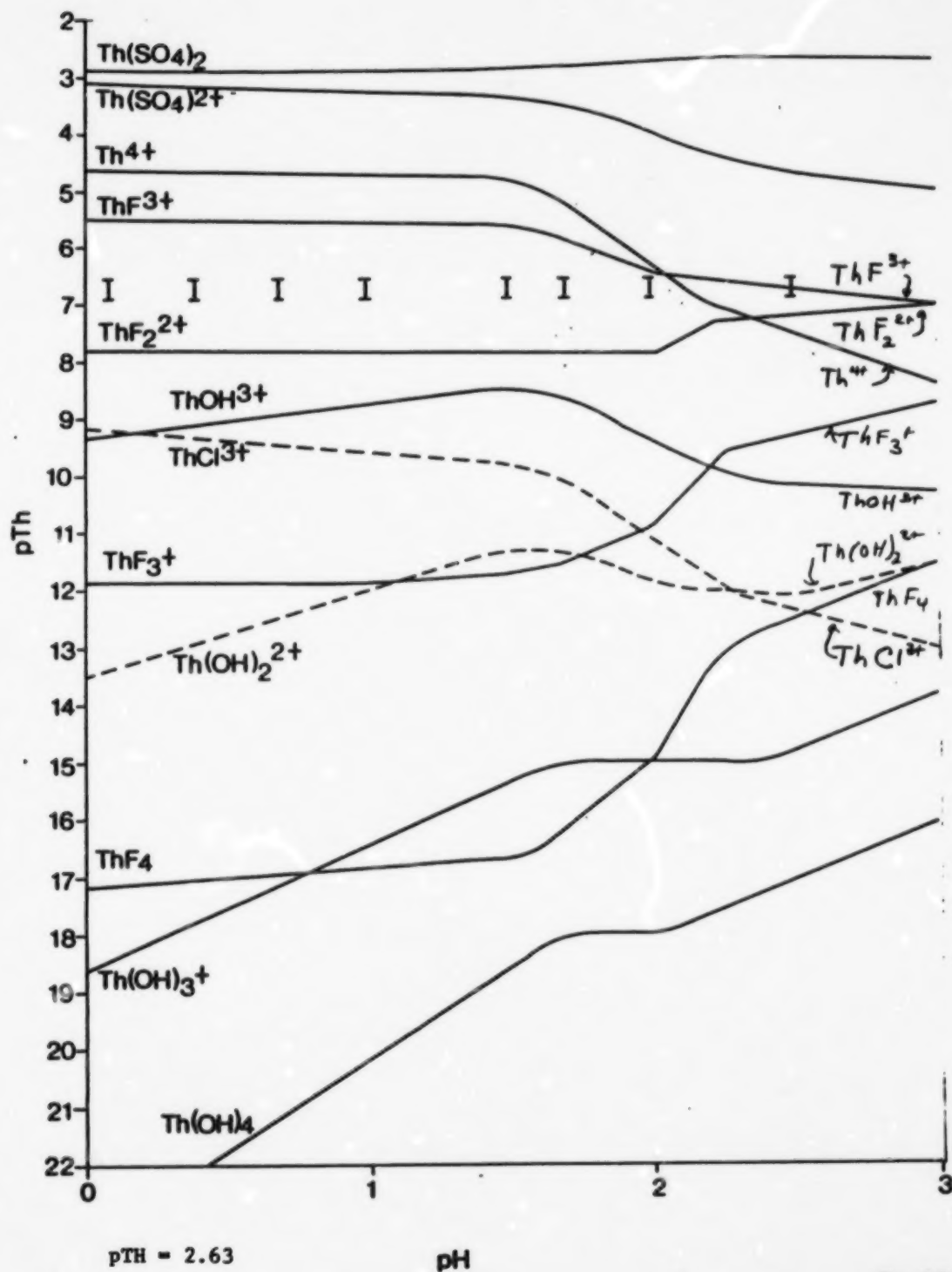


Fig.A9e. Thorium

FIG. A.9 (cont'd) Bjerrum Diagram for Water 1

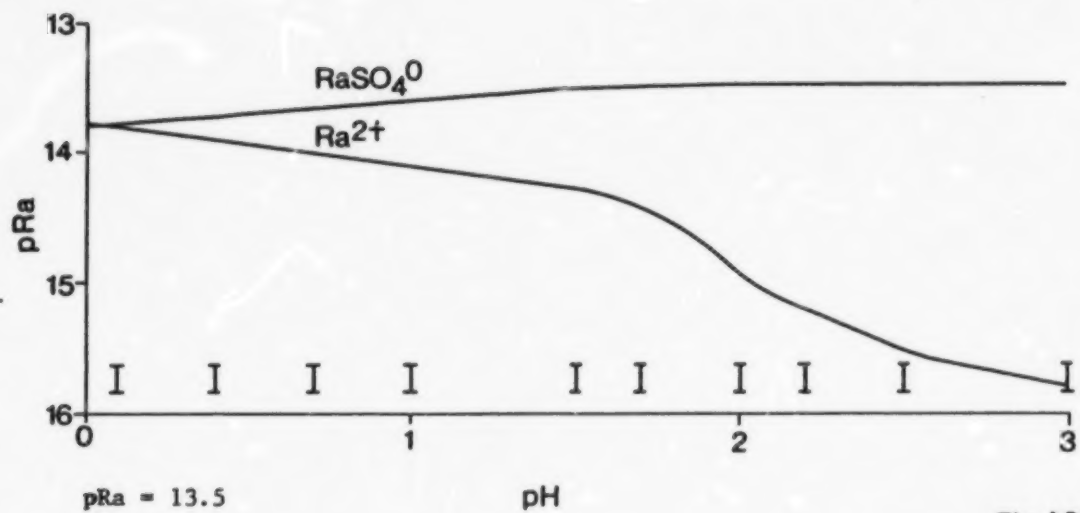


Fig.A9f. Radium

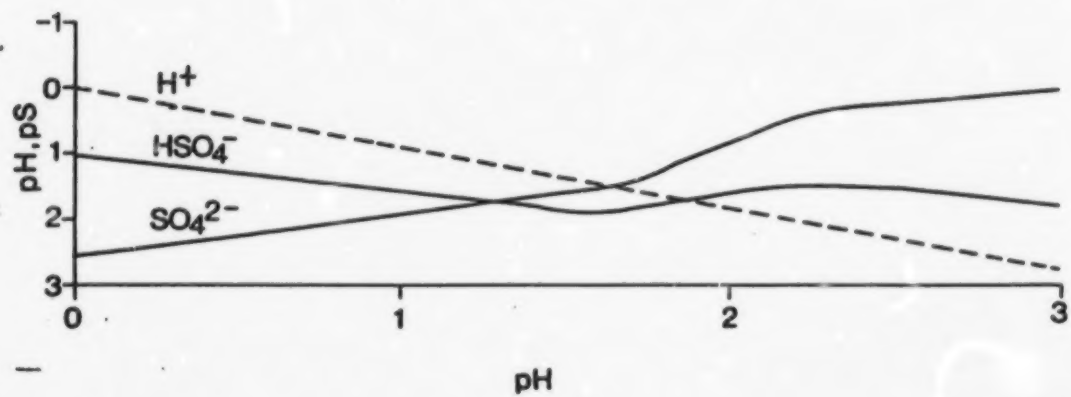


Fig.A9g. Sulfate

FIG. A.10 Percentage Composition of various metal-ligand forms for Water 1 (Actual pH = 0.7)

WATER 1.

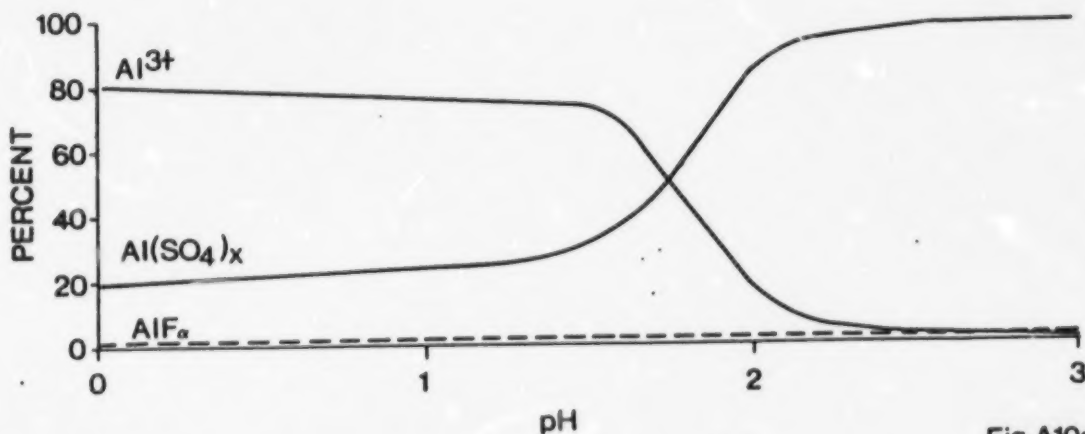


Fig.A10a. Aluminum

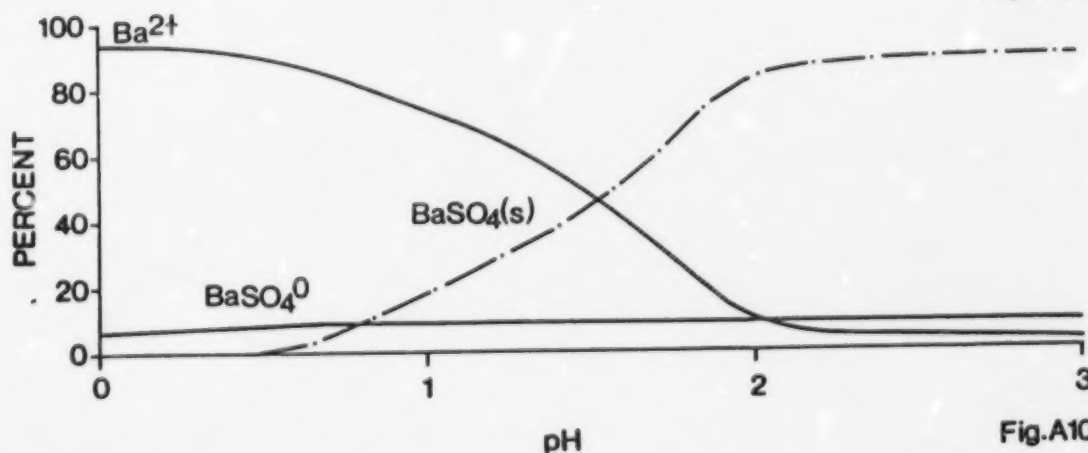


Fig.A10b. Barium

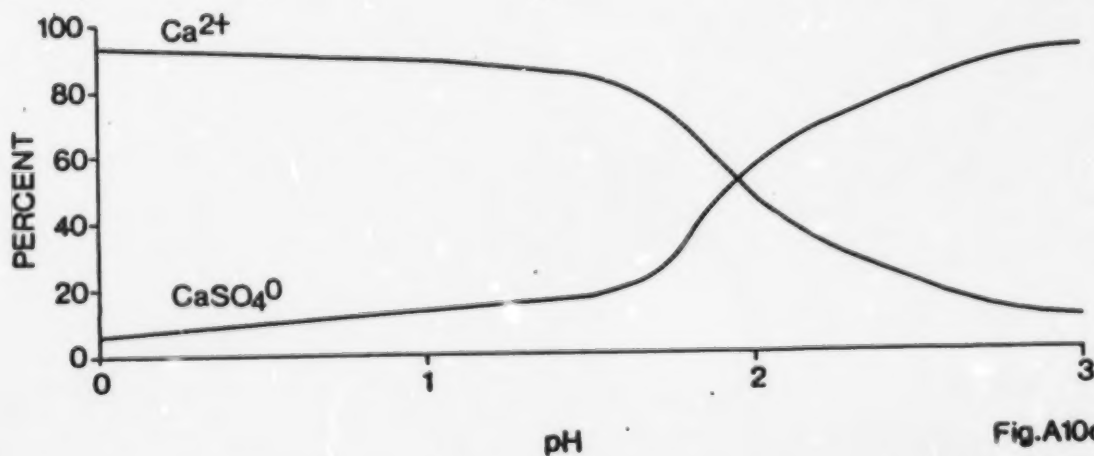


Fig.A10c. Calcium

FIG. A.10 (cont'd) Percentage Composition of various metal-ligand forms for Water 1

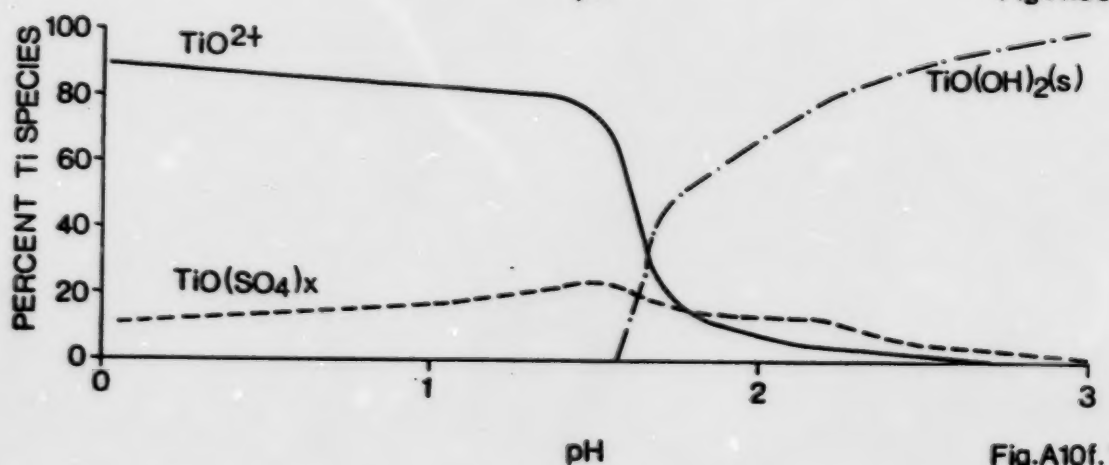
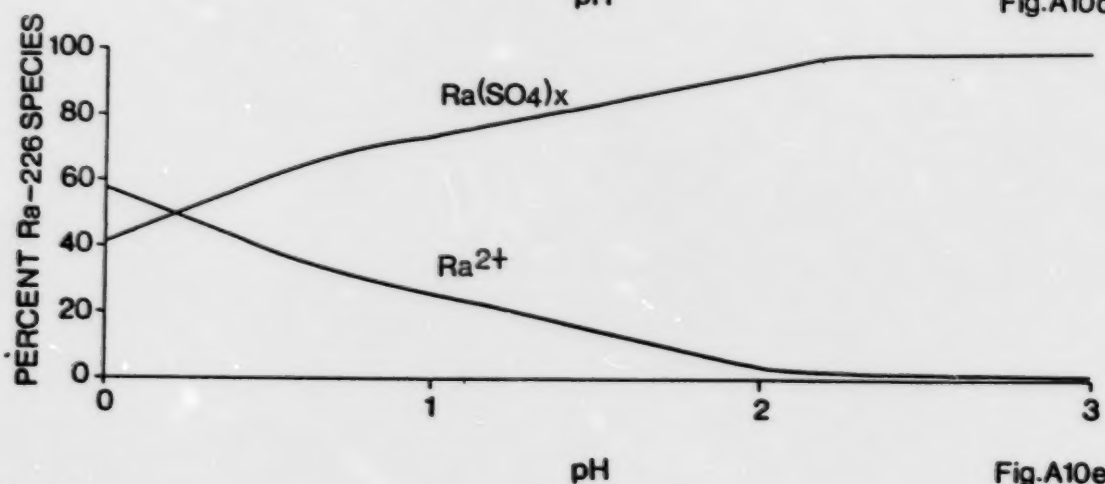
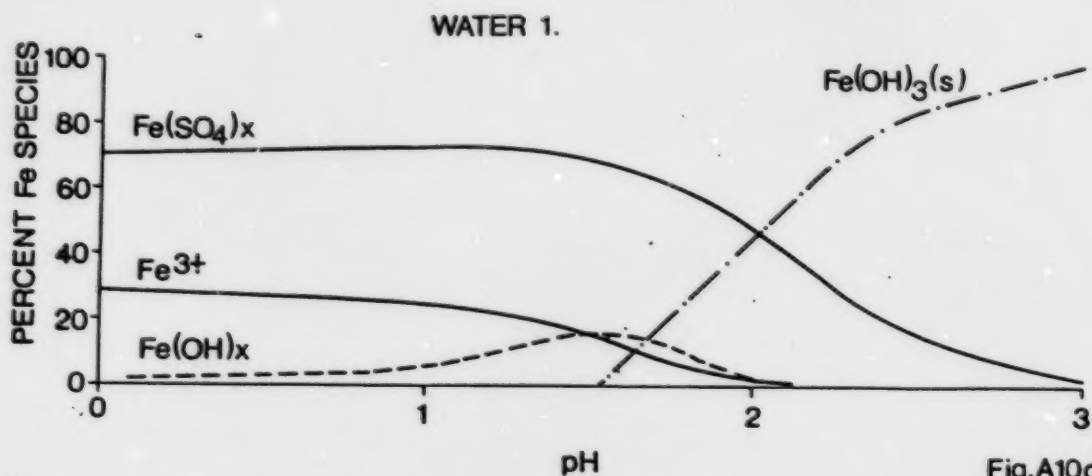


FIG. A.10 (cont'd) Percentage Composition of various metal-ligand forms for Water 1

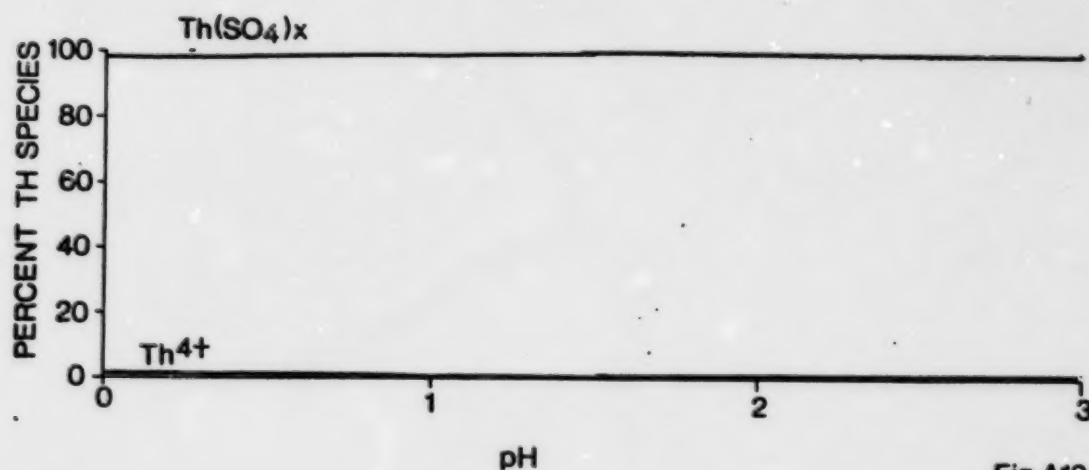


Fig.A10g. Thorium

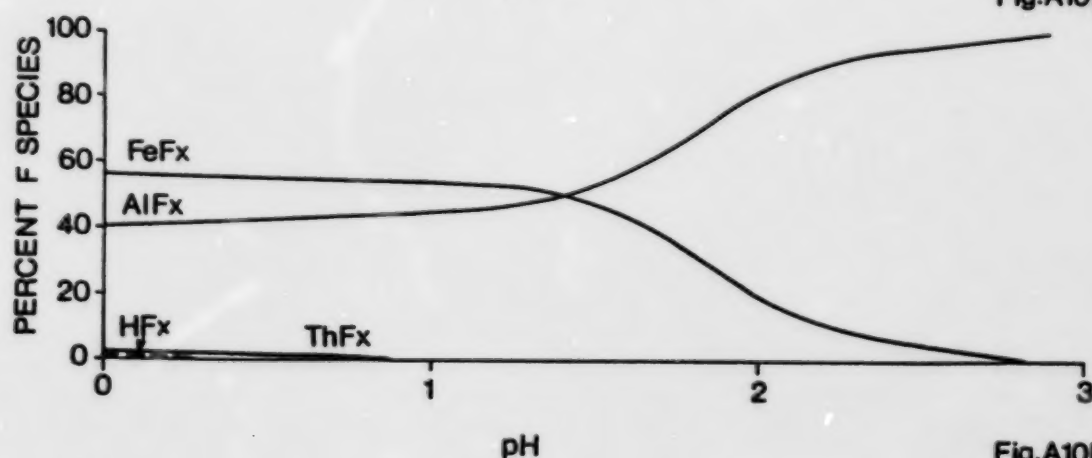


Fig.A10h. Fluoride

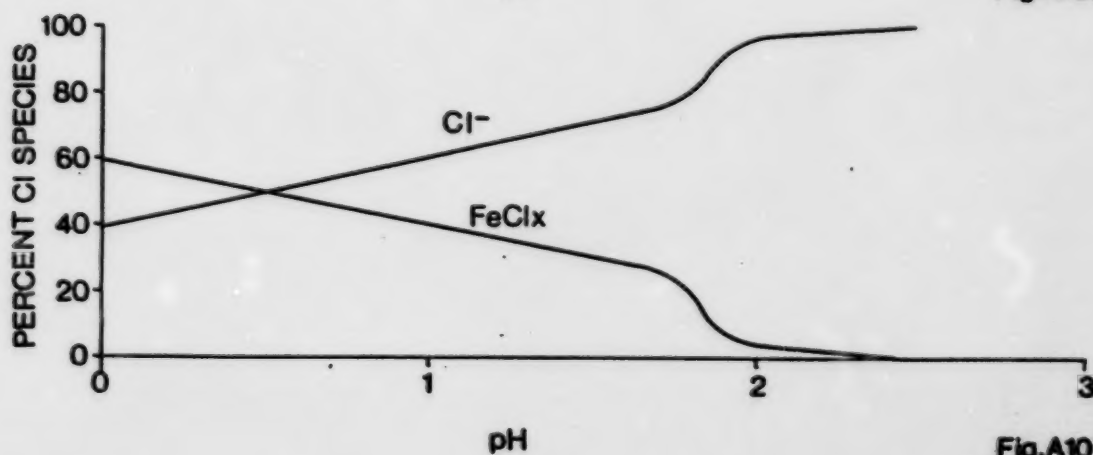


Fig.A10i. Chloride

FIG. A.10 (cont'd) Percentage Composition of various metal-ligand forms for Water 1

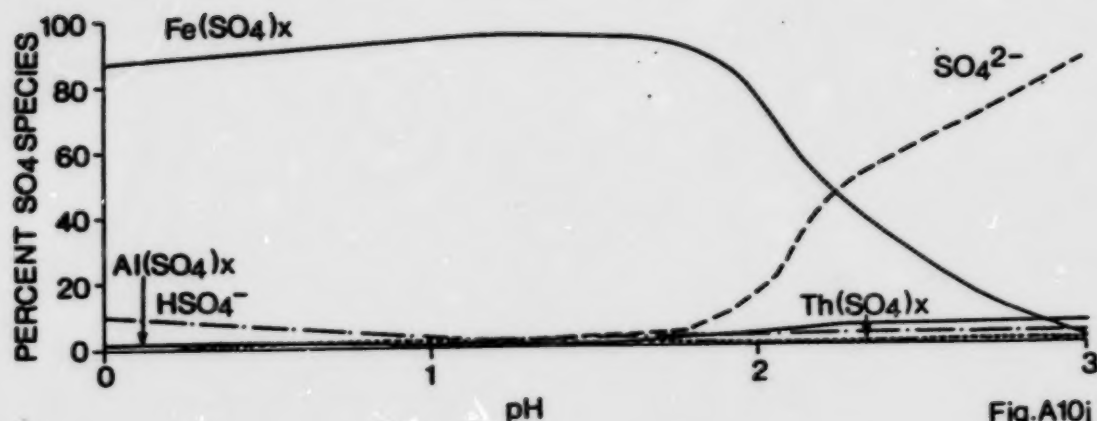


Fig.A10j Sulfate

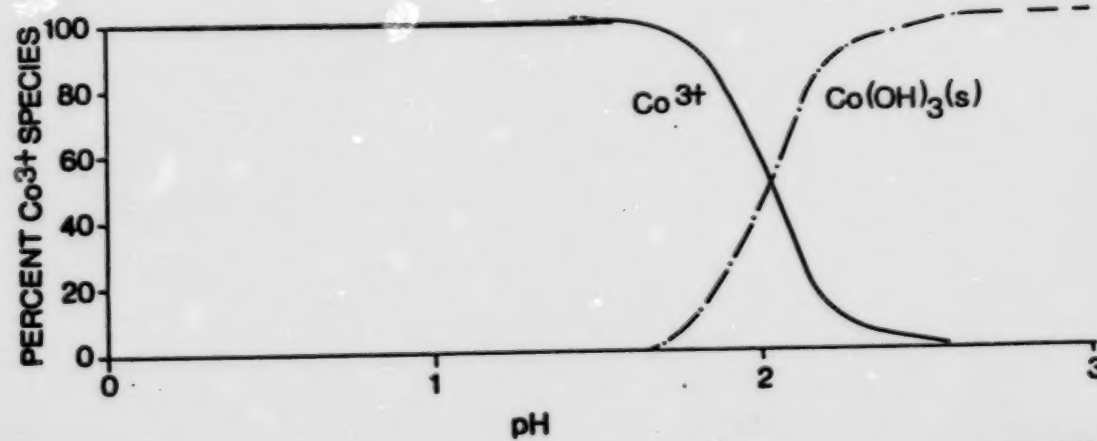


Fig.A10k. Cobalt

FIG. A.11 Bjerrum Diagram for Water 6 (Actual pH = 2.3)

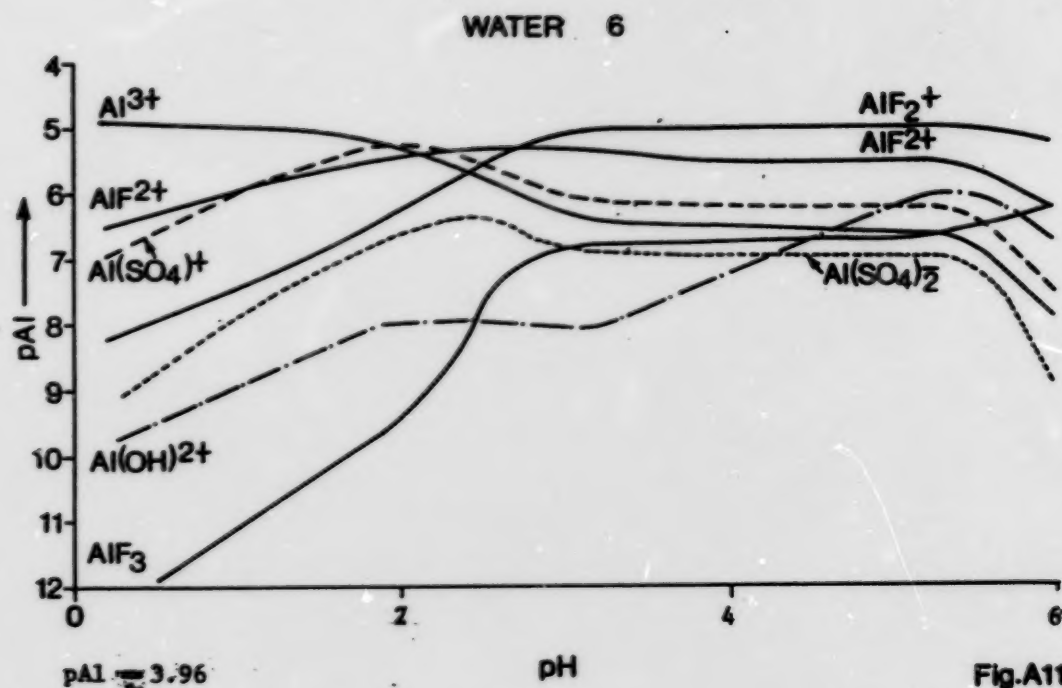


Fig.A11a. Aluminum

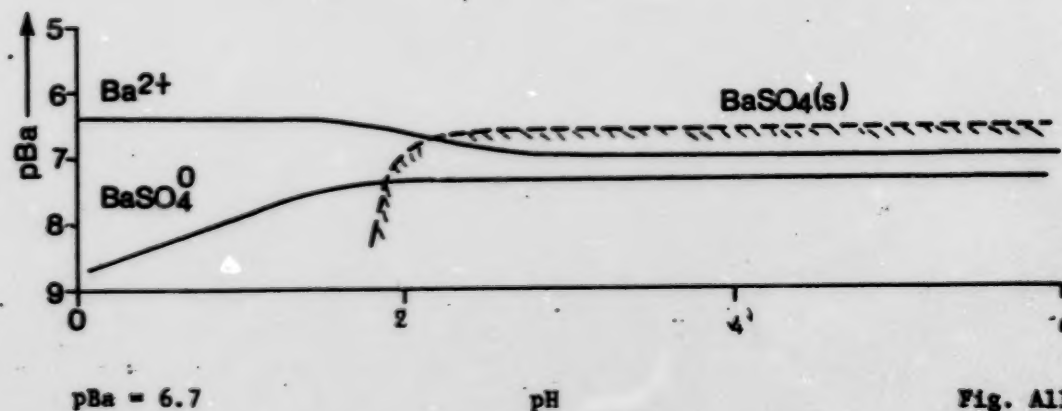


Fig. A11b. Barium

FIG. A.11 (cont'd) Bjerrum Diagram for Water 6

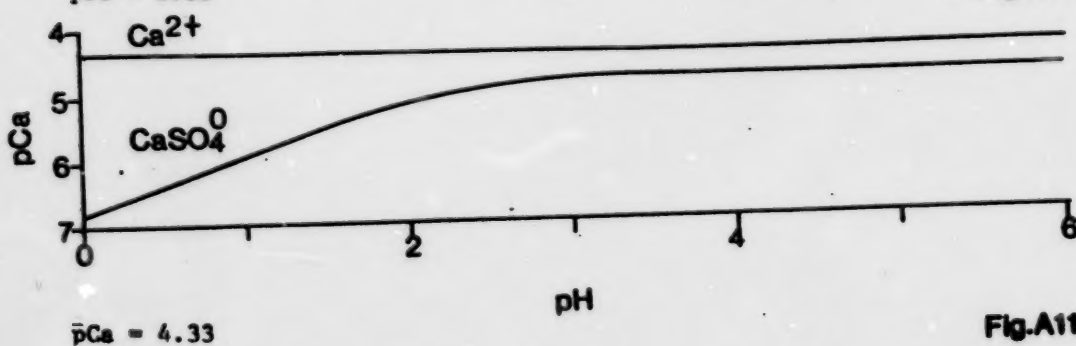
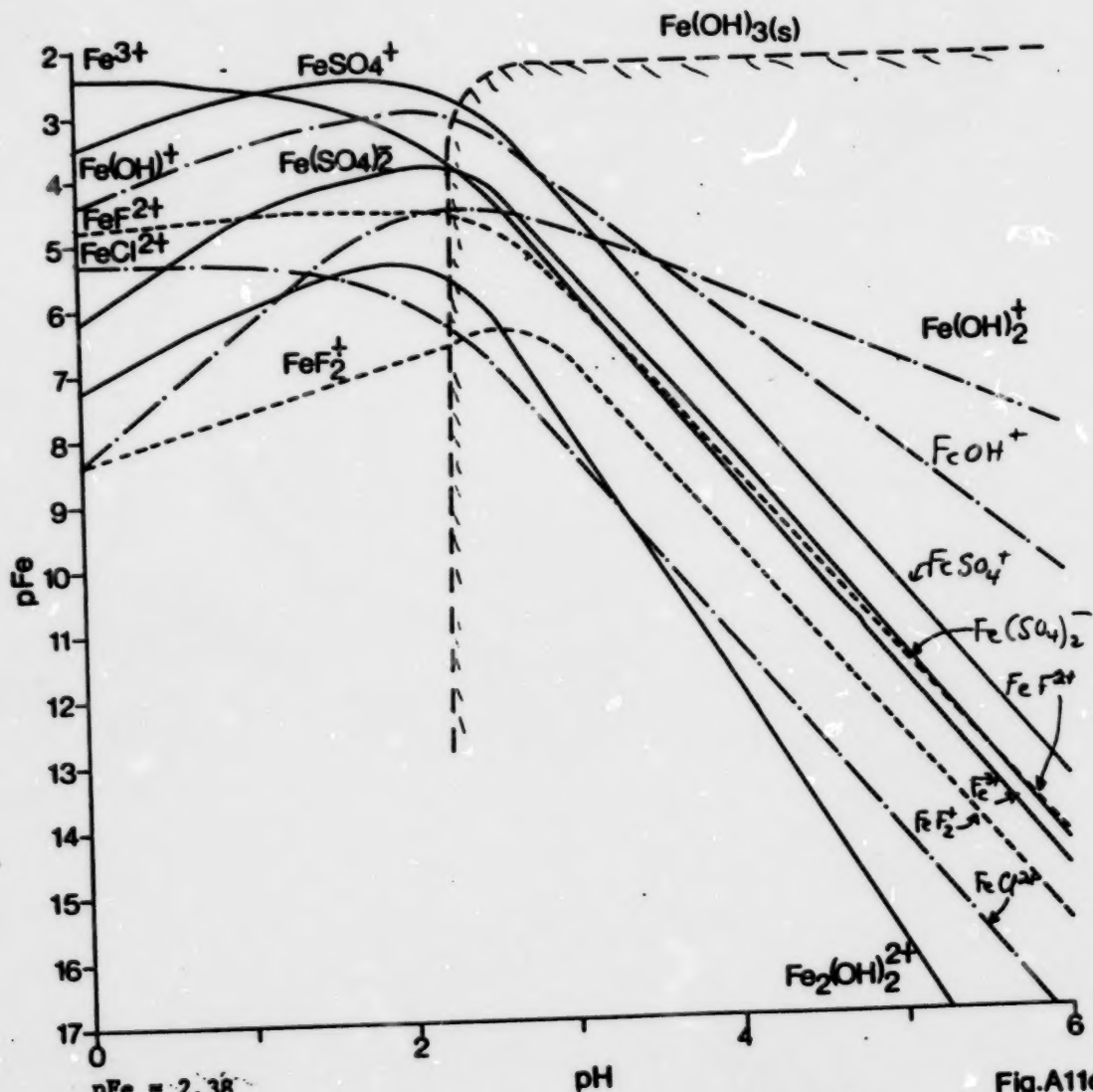
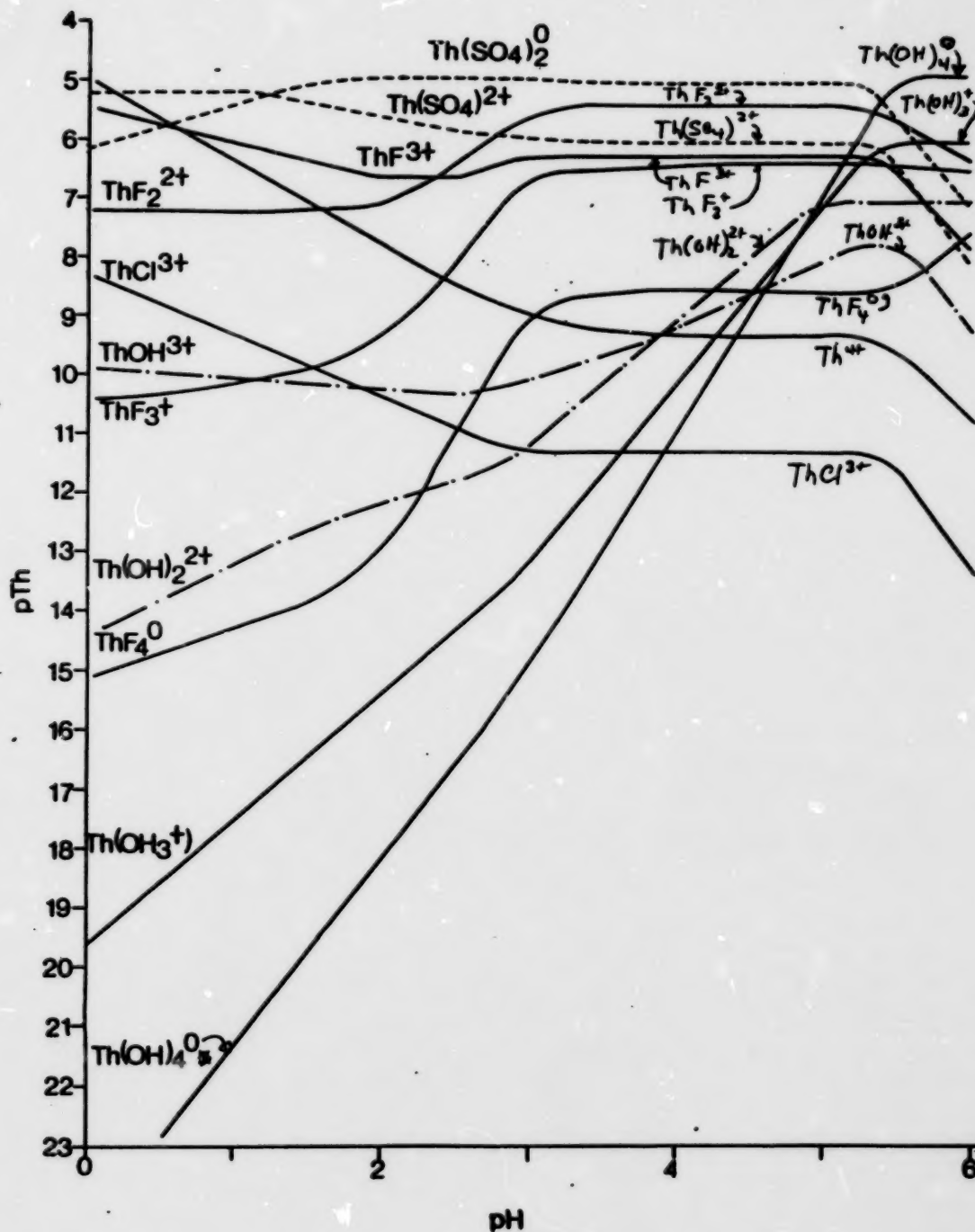


FIG. A.11 (cont'd) Bjerrum Diagram for Water 6



pTh = 4.9

Fig.A11e. Thorium

FIG. A.11 (cont'd) Bjerrum Diagram for Water 6

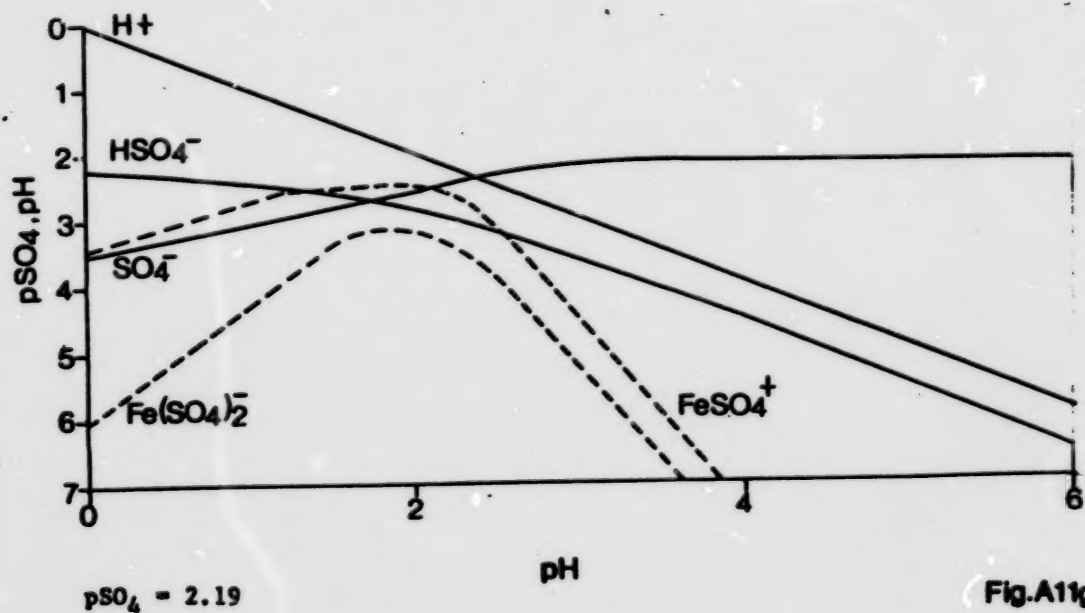
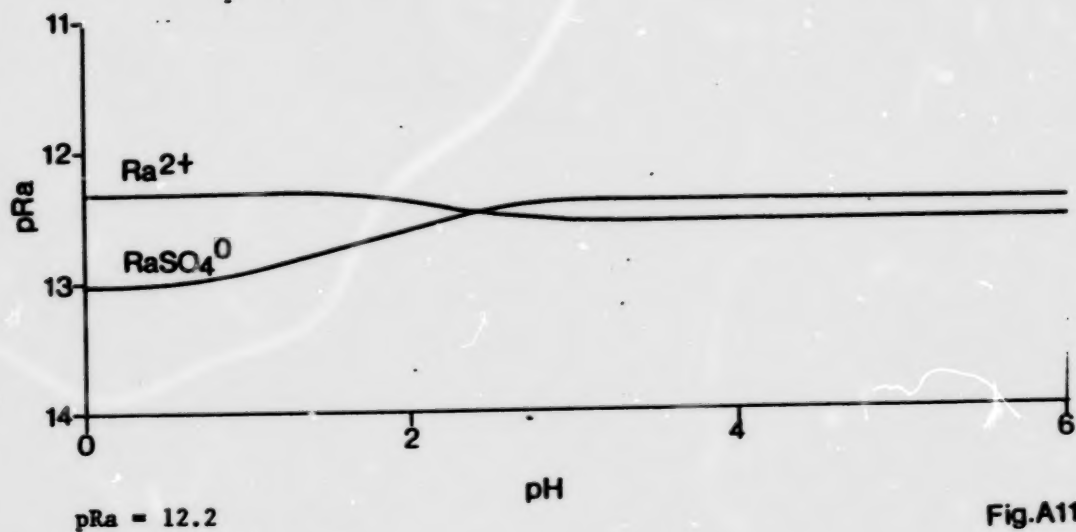


FIG. A.12 Percentage Composition of various metal-ligand forms for Water 6

WATER 6

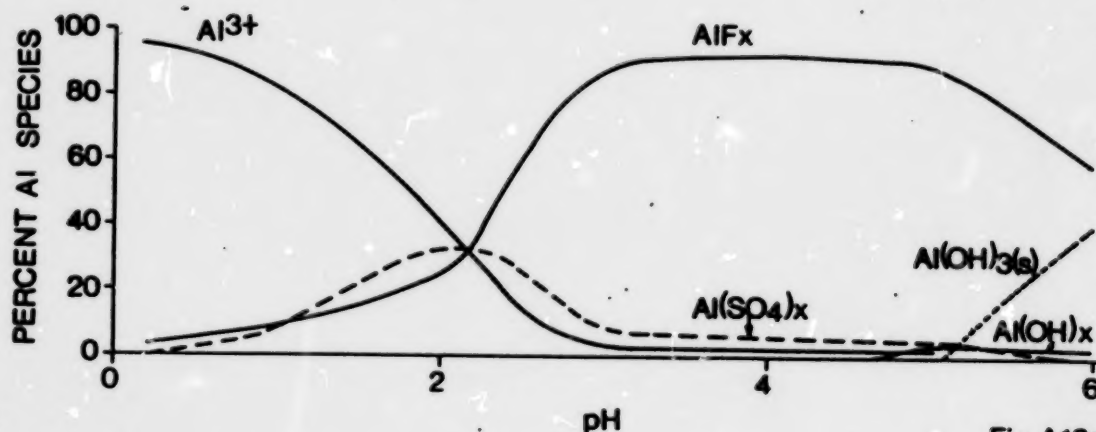


Fig.A12a. Aluminum

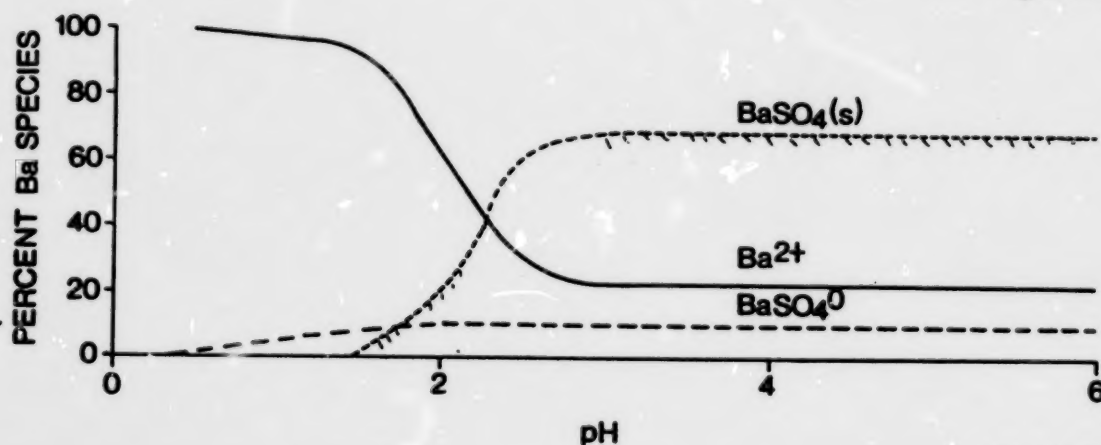


Fig.A12b. Barium

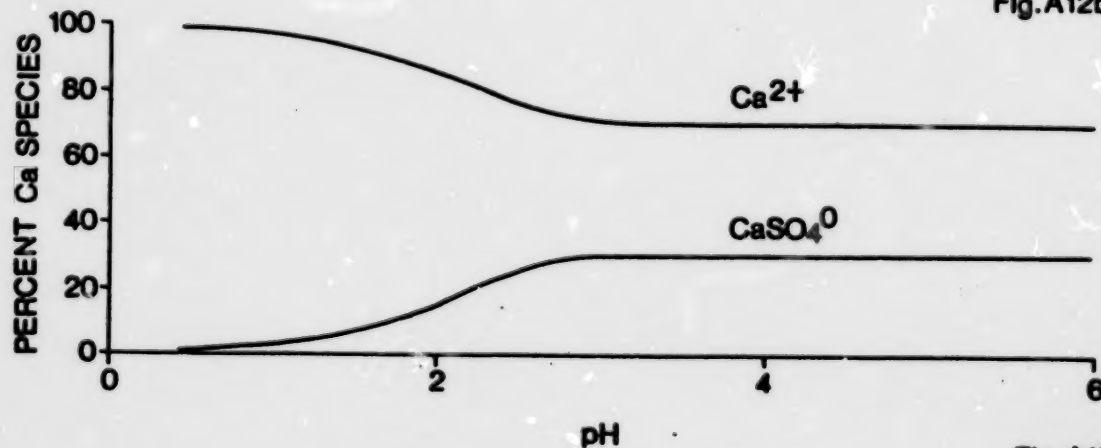


Fig.A12c. Calcium

FIG. A.12 (cont'd) Percentage Composition of various metal-ligand forms in Water 6

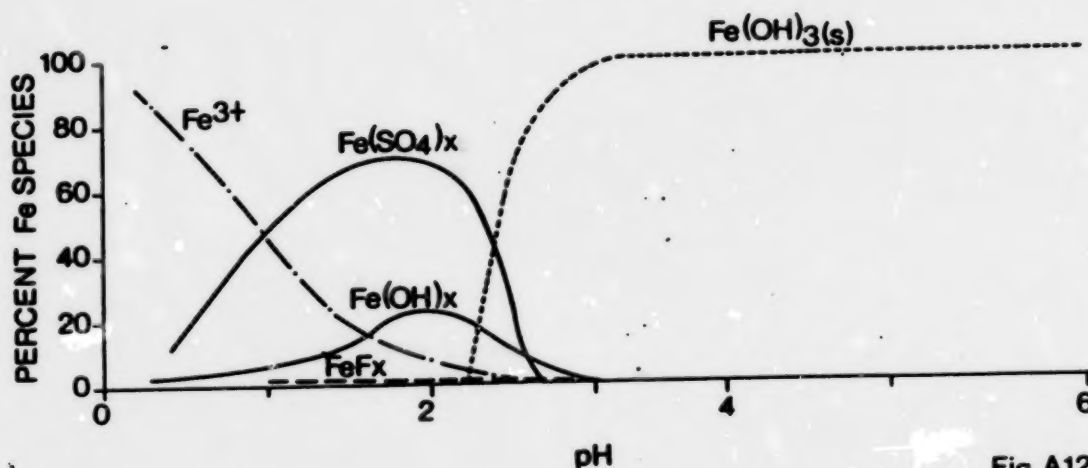


Fig.A12d. Iron

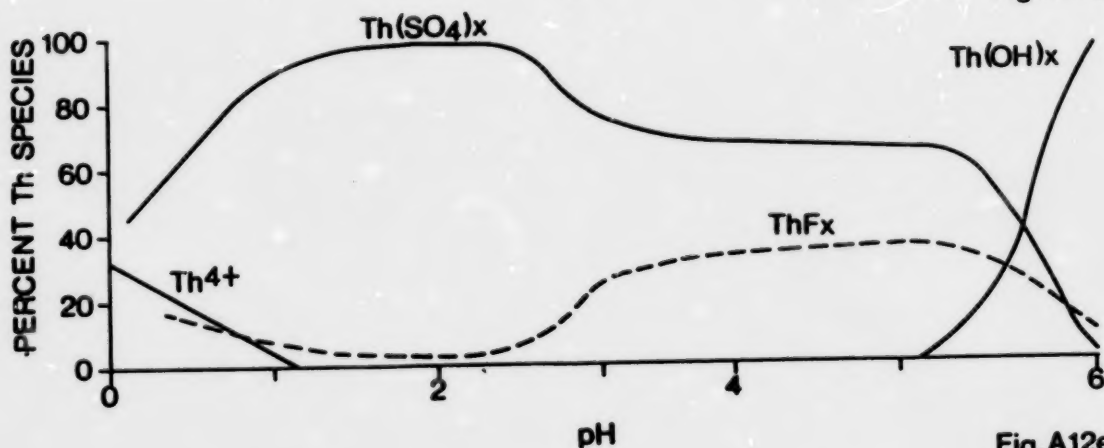


Fig.A12e.Thorium

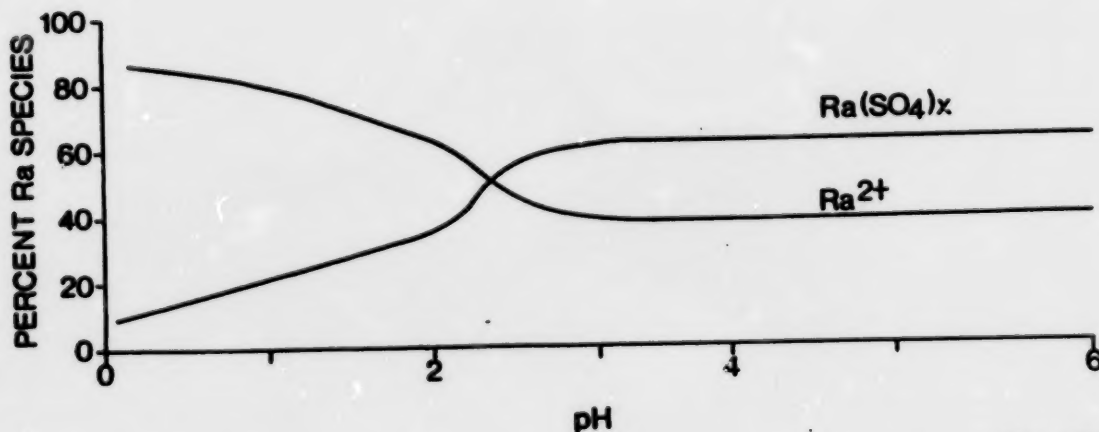


Fig.A12f. Radium

FIG. A.12 (cont'd) Percentage Composition of Various metal-ligand forms in Water 6

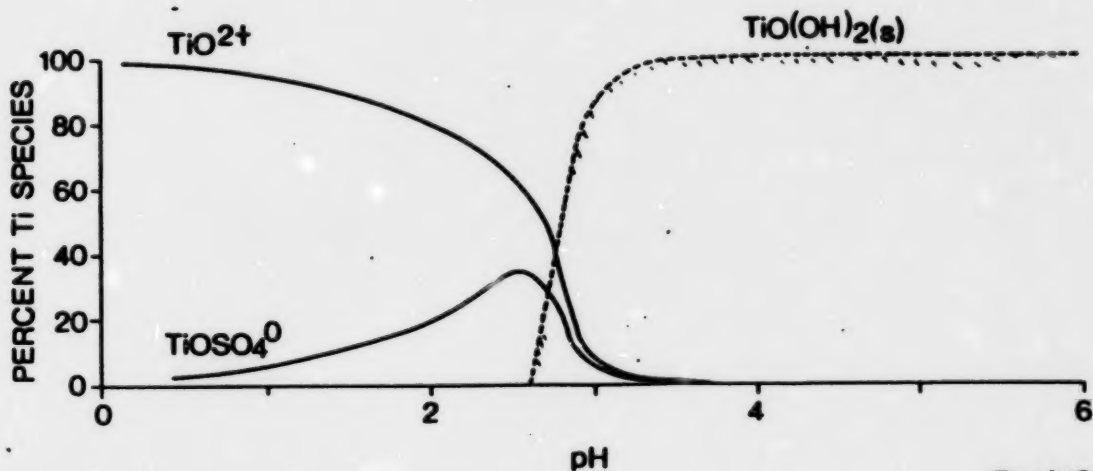


Fig.A12g. Titanium

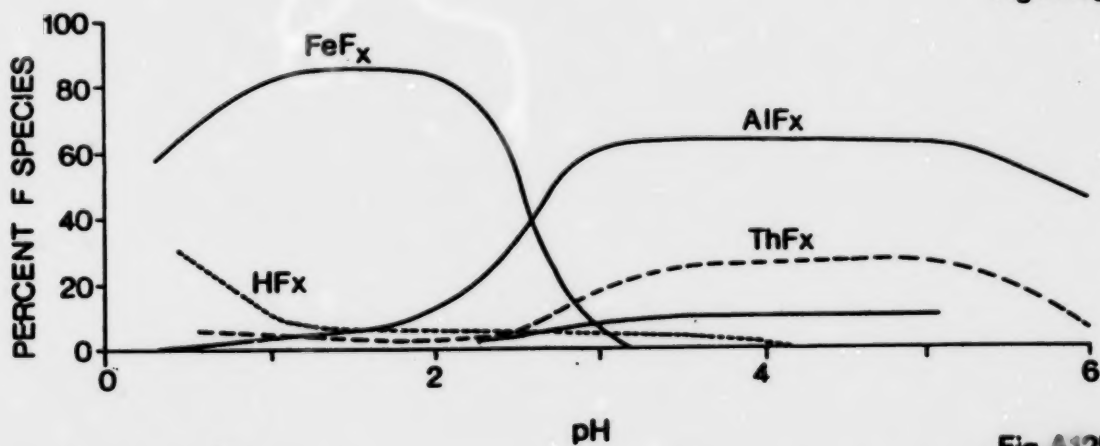


Fig.A12h. Fluoride

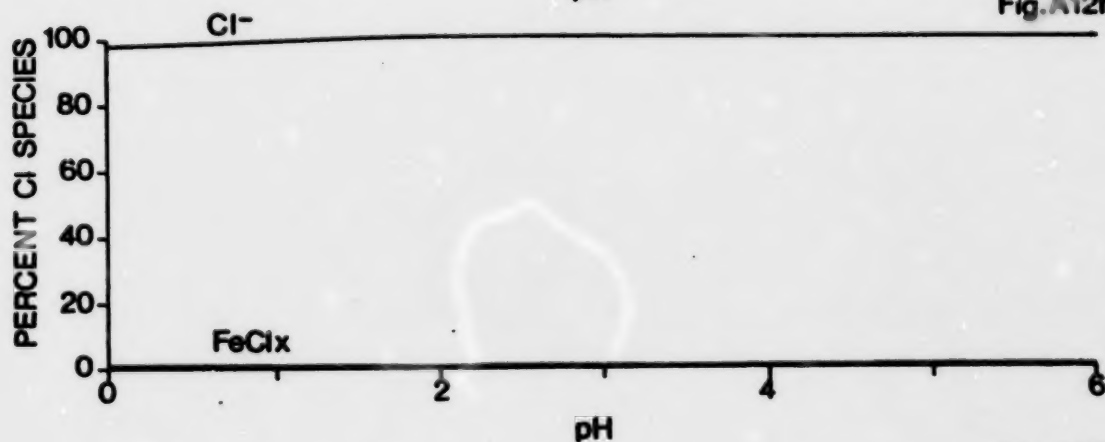


Fig.A12i.Chloride

FIG. A.12 (cont'd) Percentage Composition of various metal-ligand forms in Water 6

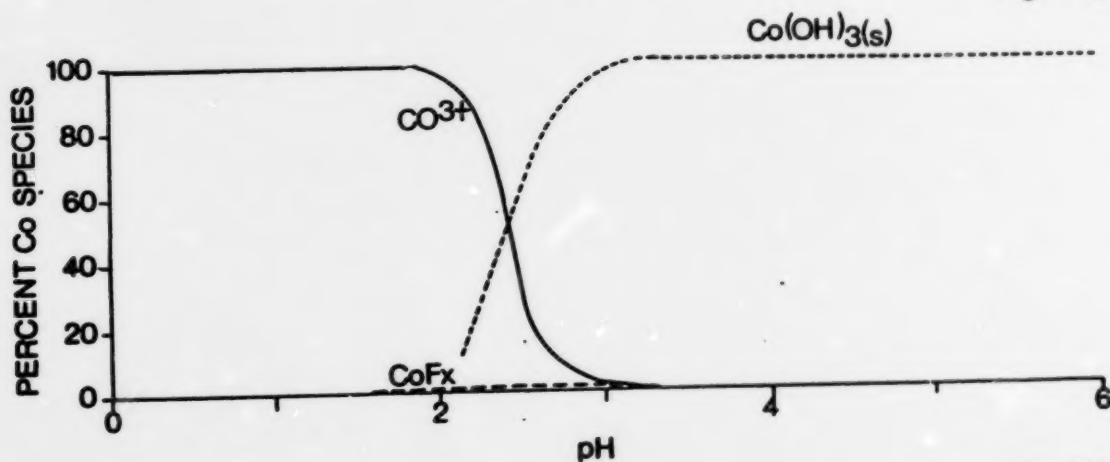
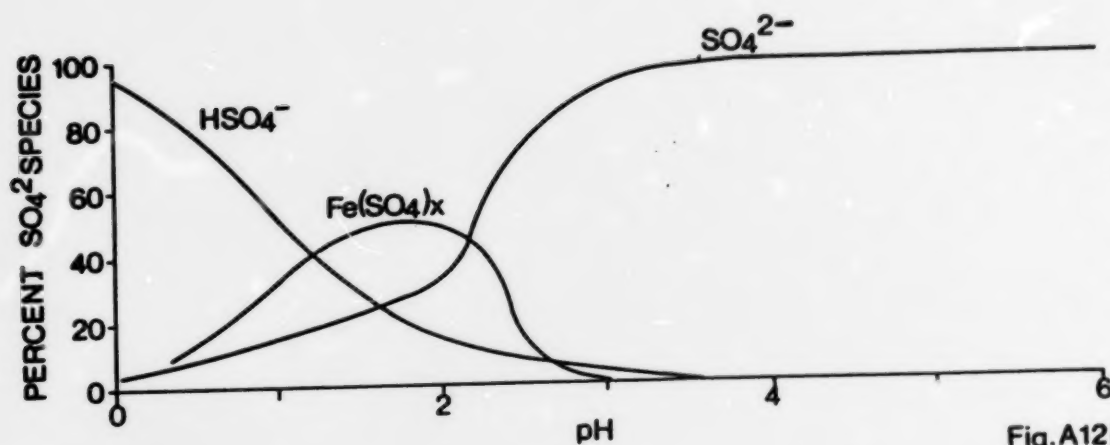
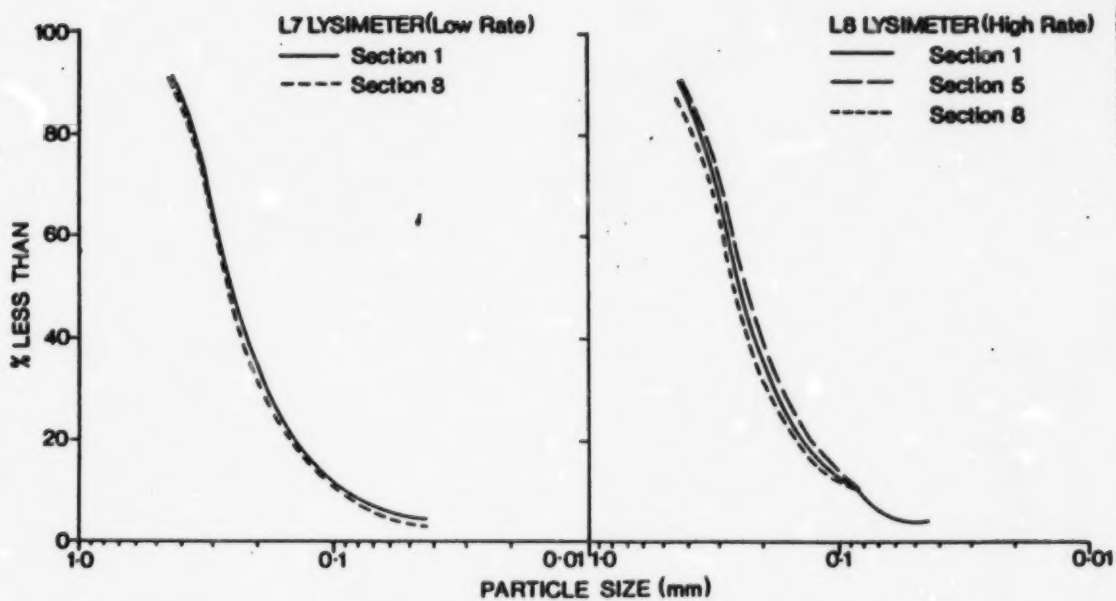


FIG. A.13 : Particle size distribution of lysimeter solids



FigA13. PARTICLE SIZE DISTRIBUTION OF LYSIMETER SOLIDS

A

APPENDIX A

CHARACTERIZATION OF LEACHATES AND TAILINGS

A.1 Chemical Controls on Leachate from Experiment I

Representative leachate samples from the last 1.5 years of the study were analyzed for all major cations and anions and various trace metals. The actual samples analyzed are given in Table A.1. The last 1.5 years correspond to the period when a major shift in geochemistry occurred - the pH of the low rate lysimeter increased from 0.7 to 1.5, TDS concentration decreased from about 200 g/L to near 20 g/L while the pH of the high rate lysimeter increased from 2.4 to 3.1 and its TDS concentration decreased from 1.5 g/L to 0.15 g/L. Measured concentrations on the leachate are given in Table A.1b. Cations are measured by ICAP while anions are measured by Ion Chromatography.

In general, each leachate sample is an iron sulfate solution reflecting the fact that its composition is dominated by the aerobic oxidation of pyrite minerals (by the bacteria T. ferroacans). Aluminum and potassium are the next most abundant cations; it is suggested that they originate from proton attack upon aluminosilicates such as K-feldspar. Calcium and magnesium are the next most abundant cations; they may originate from residual sulfates formed during milling but it is more probable that they also result from proton attack upon aluminosilicates. The negligible concentration of sodium suggests that sodium aluminosilicates are not present in the lysimeter solids. The high concentrations of copper and nickel suggest that oxidation of chalcopyrite (CuFeS_2) and of a nickel sulfide may be occurring; however the quantity of metal sulfide is small relative to pyrite. The concentration of titanium may originate from proton attack on titanium minerals such as rutile (TiO_2) or titanite (CaTiSiO_5). The concentration of other cations (Ag, Ba, Be, Cd, Co, Cr, Mn, P, Pb, Sr, Th, V, Zn) will have a negligible effect upon solution pH although the potential control upon radium-226 transport of cations such as Ba and Pb cannot be disregarded.

Sulphate is the dominant anion. Nitrate is present in significant amounts in certain samples due to addition of nitric acid for sample preservation; nitrate is assumed herein to be negligible. Detection limits of ion chromatography when the samples are diluted

1:100 to allow measurement of sulfate preclude substantial statements about the patterns of phosphorus and nitrate in these waters. The concentrations of orthosilicic acid and fluoride result from acid attack upon aluminosilicates; chlorides result from similar attack. The concentration of TOC and ammonia result from biomass formation during pyrite oxidation; CO_2 and N_2 from air or that dissolved in the applied water and organic compounds in distilled water are possible sources of carbon and nitrogen. It is doubtful that any carbon of significance is available in the lysimeter solids although organics are applied during milling - the work of Ritcey and Silver (1980) suggests that such compounds are not significant in pyrite oxidation reactions. Furthermore any such compounds are expected to be present only in trace amounts, 20 years after discharge to the tailings pile.

The majority of the parameters measured in the leachate from the 20 year old tailings by the WTC are TDS, pH and radionuclides (Th 230, Ra-226, Pb-210, Th-232, Th-228). Assuming that the chemistry of the radionuclides in the leachate is controlled by solid-solution equilibria of major cations and anions controlling the pH, buffering capacity and biochemistry of leachate waters, it is essential to describe the ability of analytical chemistry to characterize the precision of measurements of total concentrations of anion cations and of their major metal-ligand speciation. The precision of analytical chemistry is now checked by comparing (i) measurements of TDS made by various laboratories and (ii) the electroneutrality of the anionic-cationic balances. (see section 4.4.1). Then the speciation of the major ions and metal-ligand complexes are described in section 4.4.2. This section concludes by examining stoichiometric concepts for describing the pyritic oxidative metabolism of the lysimeters (section 4.4.3) and with a few comments on correlations between the cationic-anionic characteristics of the leachate and the specific activity of various nuclides.

Figure A.1 gives a comparison for the high rate lysimeter of measured TDS (IEC Beak Laboratory) and the TDS calculated from the ICAP (cations) and ion chromatography (anions) analysis by Barringer. These TDS balances include the dissolved solids derived from HNO_3 addition for acid preservation. The calculated values for TDS are consistently less than measured values. The degree of difference is not a function of concentration. A plot of data suggests an equally random difference throughout the wide range of concentration. The plot of TDS measured by the WTC before HNO_3 addition and that calculated from the anion-cation analysis of Barringer (Figure A.2) suggests

increased deviation from the 1:1 relationship compared to that of Figure A.1. The increased deviation either results from the values of calculated TDS (a large number minus a large number) or different concentrations in TDS between the time that the samples were first taken and analyzed for TDS (by the WTC in 1980-81) and reanalyzed (by IEC Beak in Jan. 1983). Due to the addition of the HNO_3 for sample preservation, in the high rate lysimeter samples, a direct comparison of the two sets of TDS measurements by the two different laboratories is most appropriate on the leachate from low rate lysimeters because they did not have significant quantities of HNO_3 added as preservative.

The calculated TDS for the low rate lysimeter again is lower than that measured by the WTC (see Figure A.3). The effect of HNO_3 on these samples is less than 5% for the 2 samples to which HNO_3 was added. Hence the difference is not caused by preservatives.

The difference could be caused by precipitation reactions during the time between analyses for TDS (1-2 years ago) and the ICAP-IC measurements for cations and anions. A comparison between TDS measured by IEC Beak and those measured by the WTC (Figure A.4) suggest that the WTC measurements are slightly and consistently higher than those of IEC Beak; this allows for some degree of precipitation but the difference is quite small compared to the difference between measured and calculated TDS. The differences between sets of TDS measurements can easily be attributed to analytical results from two different laboratories.

The difference between ICAP-IC measurements and TDS measurements have also been observed by IEC Beak on other waters; particularly groundwaters. It is possible that part of the measured TDS are water molecules which are bound to a metal and which do not evaporate during the drying process used for TDS analysis. For example, hydrated iron is octahedrally coordinated with 6 water molecules as innersphere complexes. For a water containing 56,000 mg/L Fe (i.e. 1M), there are 108,000 mg/L of water molecules associated with the iron (i.e 6 M $\text{H}_2\text{O}/\text{M Fe}$). One needs about 30,000 mg/L TDS in the form of water to close the balance. This would be supplied if 1/3 of the water molecules coordinated with iron did not evaporate during drying. Another possibility is the formation of ferric hydroxo-polymers which do not break up during drying. The existence of such compounds is a matter of debate at pH 0.8-1.5. The calculations given in the next section suggest that $\text{Fe}_2(\text{OH})_2^{2+}$ is not a probable species at these low pH's.

Another possible error is that sulfate is inaccurately measured. For oxidation of pyrite, a Fe/S ratio of 0.5 is expected. For the low rate lysimeter, the ratio varies from 0.5 to 0.75 while it varies from 0.1-0.65 for most of the leachate from the high rate lysimeter. This would suggest that the sulfate concentration is too low in the low rate lysimeter and that some Fe^{3+} is precipitating out of solution in the high rate lysimeter (i.e. for those samples where the Fe/S is less than 0.5). It is plausible that incomplete oxidation of FeS_2 is occurring, yielding an SO_3^{2-} ion which is not picked up in the normal domain of ion chromatography. But this possibility is counter to the thermodynamics of the redox reaction - oxidation of sulfide should be complete at a much lower redox potential than that of Fe^{2+} .

Another method for checking the sulfate measurements is their comparison with acidity measurements and electroneutrality calculations. The sum of sulphate plus nitrate agrees with measured acidity (measured to a pH 4.5 operationally defined end point) for the high rate lysimeter (Figure A.5), although most of the measurements of acidity are somewhat higher than levels of SO_4^{2-} and NO_3^- would suggest. Nitrate is included in the diagram because substantial quantities of nitrate were added to the samples for preservation. When the effects of HNO_3 are removed from "measured values", the deviation from a 1:1 relationship between measured acidity and SO_4^{2-} (see Fig. A.6) for the high rate lysimeter does not increase substantially, although the scatter about the 1:1 line has increased. For the low rate lysimeter (see Fig. A.7), measured acidity is consistently higher than measured sulphate by 10-20%. This suggests that sulphate concentrations are low, provided that an operationally defined end point of 4.5 does not substantially overshoot neutralization of acidity incorporated in the proton complexed with sulfate.

The electroneutrality balances present either a similar or a different picture depending upon ones interpretation of the redox chemistry of iron and the speciation of SO_4^{2-} . Assuming that Fe is all as Fe^{3+} , the sum of cations is larger than the sum of anions for the low rate lysimeter; a less consistent but similar pattern is observed for the high rate lysimeter. Samples showing negative values for cations in the high rate are associated with samples to which HNO_3 was added and/or samples in which Fe^{3+} precipitation is probable (the Fe/S ratio is less than 0.5). If Fe^{2+} is assumed to be the form of iron, the sum of cations is less than the sum of anions for the low rate lysimeter. But if the actual complexation of sulphate reacting with H^+ is considered, the sum of the anions decreases

substantially. A mixed pattern is observed comparing total anions and total cations (based upon Fe^{2+}) for the high rate lysimeter (see Table A.2).

Another way to check the lack of balance for measured versus calculated TDS is the use of volatile dissolved solids (VDS). VDS is often used as a measure of organic carbon. But TOC is less than 1% of TDS in all these waters; hence VDS must represent another material. VDS is the difference between TDS left after evaporation at 105°C and TDS left after drying at 450°C . The only probable explanation is loss of waters of hydration, iron or sulfate during this drying process. Iron and sulphate are the only probable cation and anion because 99% of calculated TDS is due to these two materials. The loss of iron or sulphate at 450°C is improbable. Waters of hydration are then the only explanation. When VDS is added to anions + cations, this quantity approximately equals the measured TDS for all waters.

Accordingly, it is concluded that the lack of balance between measured TDS and calculated TDS is due to incomplete loss of waters of hydration of Fe^{3+} . Hence the TDS values measured throughout this project are about 30% high. Furthermore for tailings whose pH is less than 3, estimates of Fe and SO_4 concentrations can be then made from TDS provided the values are decreased for the waters of hydration not lost during the measurement. Precise estimates for different waters should be made by measurement. But an estimate of the order of 30% seems appropriate for Fe- SO_4 waters. For CaSO_4 waters, it is possible that a reduction of $2(18)/(40.1+96.1+2 \times 18)$ or about 20% should be made to TDS values. The two waters of hydration are lost at 175°C ; this calculation assumes that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ forms during the drying of a gypsum water. Similar theoretical calculations are not available for the Fe- SO_4 water because no information was found on the temperature for hydrated water loss from Fe^{3+} .

To calculate the probable TDS pattern over time, one would either calculate the aqueous species in leachate waters assuming that they are dominated by the oxidation of FeS_2 and/or one could use conductivity-TDS relationships. Conductivity is a useful surrogate; unfortunately it is difficult to calculate conductivity at these high levels of TDS as the normal theory for electrical contribution of different ions to conductivity is erroneous at high ionic strength. For example, the data of Landolt-Bornstein (1950) for equivalent conductance for H^+ , HSO_4^- and SO_4^{2-} , and a calculation of the speciation of HSO_4^- - SO_4^{2-} using the method of Rossen (1973) and Lind (1970) suggest a conductance of 110

mmhos/cm whereas the observed value is much larger. According resort is made to a plot of conductivity vs TDS; this is presented in Figure A.8 for these waters. For all waters to which HNO_3 was not added, a linear relationship is observed, except for one water. The effect of HNO_3 is to displace the relationship towards a higher conductance for the same TDS. Accordingly, a TDS-conductivity relationship may be used, provided that the major charge determining species (e.g. iron sulfate or calcium sulfate) do not change.

A.2 Cation-Anion Speciation

The formation of various complexes can significantly influence the transport characteristics of cations and anions from the lysimeter. The measurement of the concentration of different complexes is difficult in solutions of several anions and cations. Hence, resort may be made to speciation calculations based upon knowledge of: (i) total concentration of anions and cations, and (ii) thermodynamic constants which describe the solubility and complexation of metal ligands solids and soluble metal-ligand complexes, respectively. Such calculations provide guidance to estimating the probable chemistry of the water but the calculation cannot be viewed as absolutely precise because actual equilibrium may not exist or because some uncertainty may exist over the value assigned to the thermodynamic constants.

The algorithm of Morel and Morgan (1972) is used herein to make speciation calculations for sample waters. The thermodynamic data is from the compilation of Sillen and Martell (1964, 1971) and Ringbom (1963) updated by a review of constants for complexes and solids of metal sulphates, fluorides and chlorides from IUPAC (1980). Constants for thorium-fluoride species are those of Beak (1982) while the constants for radium-sulfate and radium-chloride species have been recently measured by Benes et. al. (1981). The identification of a RaSO_4^0 species by Benes et. al infers that the original solubility product for RaSO_4 measured by Nikiten and Tolmatseheff (1932) is somewhat in error because they do not appear to have considered the RaSO_4^0 complex. Inclusion of the RaSO_4^0 complex gives a solubility constant for $\text{RaSO}_{4(s)}$ of $10^{-10.41}$. The adjustment to the value calculated by Nikiten and Tolmatseheft is small (their value is $10^{-10.37}$).

Ten leachates were selected for speciation calculation (see Table A.2, A.2). The leachate waters are designated by the terminology "model water" or "water". This terminology is selected to emphasize the following points that the specification of all chemical constituents in the leachate water is incomplete, (ii) that the thermo dynamic data which describe the complexation and precipitation-dissolution reactions may have errors associated with them and (iii) that the number of complexes known to form (given present day knowledge) may actually be incomplete. Waters 1 and 2, and waters 3 and 5 are the initial and final leachate samples analyzed by ICAP-IC from the low rate lysimeters (L1 and L7 respectively); water 4 is intermediate in time between 3 and 5. Similarly waters 6 and 8 and waters 9 and 10 are the initial and final leachate samples

analyzed from the high rate lysimeters (L2 and L8 respectively); water 7 is intermediate in time between waters 6 and 8 for lysimeter 2. The time period covered by the initial and final waters is the period over which the TDS decreases by an order of magnitude (see Table A.1).

Waters 1 (low rate) and 6 (high rate) are selected for calculations of aqueous chemical speciation over a pH range - the actual metal and liquid concentrations are imposed as constant but the pH is allowed to vary. These model waters would describe the actual concentrations for TDS, iron etc. which were observed in the lysimeter leachate for most of the leaching period. Ionic strength, is calculated by the computer algorithm; corrections for activity coefficients are calculated according to the Davies equation (Stumm and Morgan, 1981). The ionic strength (I) of water 1 is approximately 1.3 M. Because the Davies equation begins to give some errors at I 0.5 M, the calculations for water 1 will be viewed with some uncertainty.

Water 1 is allowed to vary over the pH range of 0-3 (see Fig. A.9). Al^{3+} dominates to pH 1.5; above pH 1.8, sulfate complexes dominate (Fig. A.9, A.10a). Ba^{2+} is stable to pH 1.5 but $\text{BaSO}_4(\text{s})$ becomes important at higher pH's (Fig. A.9a, A.10b). Iron sulfate complexes dominate from pH 0 to pH 1.8; above pH 2, iron hydroxide dominates (see Fig. A.9c, A.10d). Ca^{2+} is important to pH 1.9 above which CaSO_4^0 is most important (Fig. A.9d, A.10c). Thorium has several species of interest (sulphate, fluoride, hydroxide - see Fig. A.9c) but sulfate dominates throughout the pH range (Fig. A.10). RaSO_4^0 dominates throughout most of the pH range (Fig. A.9, A.10) while sulfate reflects the $\text{HSO}_4^- - \text{SO}_4^{2-}$ speciation predicted by a $\text{pK} = 1.9$ (Fig. A.9). Iron sulfate is the dominant species over much of the pH range (Fig. A.10). The $\text{TiO}(\text{SO}_4)_x$ complexes are of some importance, but the 2^+ complex is most important below pH 1.5 while TiO^{2+} precipitates above pH 1.7 as the hydroxide (Fig. A.10). Co^{3+} (the assumed oxidation state of Co) precipitates as the hydroxide at pH 2 (Fig. A.10). Fluoride is tied up with aluminum and iron, despite the much lower concentrations of aluminum (Fig. A.10h). Iron chloride complexes are important below pH 0.5 (Fig. A.10i).

For water 6 (the high rate lysimeter; actual pH = 2.3 at time of sampling), several shifts in speciation are noted. Some of the shifts occur because a wider pH range (0-6) is used in the titration. Aluminum fluoride complexes are much more important (Fig. A.11b, A.12b) which $\text{BaSO}_4(3)$ precipitates at a slightly higher pH. (Fig. 4.4.7b, 4.4.8b).

Aluminum hydroxide is predicted to precipitate at pH 5). For iron, $\text{Fe}(\text{OH})_3(\text{s})$ precipitates at a higher pH while $\text{Fe}(\text{SO}_4)$ complexes are less important over the pH range of 0 to 2 - $\text{Fe}(\text{OH})$ complexes and free Fe^{3+} increase in importance. Water 6 also has sufficiently less sulfate to allow CaSO_4^0 to be much less important (Fig. A.11d, A.12c) than in water 1. Sulfate species remain the dominant form of Th (Fig. A.11e, A.12e) although fluoride species assume some importance in the pH 3 to 6 range. Ra^{2+} and RaSO_4^0 are of equal importance (Fig. A.11f, A.12f) - the proportion of Ra^{2+} as RaSO_4^0 decreases from water 1 to water 6 because of the reduced sulfate concentration. Similarly the proportion of sulfate complexed with Fe^{3+} is substantially less in water 6 (Fig. A.11g, A.12k). TiO^{2+} and Co^{3+} precipitates at a higher pH (see Fig. A.12g, A.12k respectively). While thorium fluoride complexes are of importance in fluoride chemistry (Fig. A.12h), iron complexes of chloride are essentially unimportant (Fig. A.12i).

The total concentrations measured in each model water are given in Table A.3 as pC (i.e. pC - minus the log, base 10, of the concentration in moles/L). Model water 4 has the same concentrations as those actually measured except that the sulfate concentration is reduced from the actual value of $\text{pSO}_4 = 0.198$ to $\text{pSO}_4 = 1.53$. This model was used for most of the calculations; a few calculations are given for the actual leachate sample which is designated as model water 4*.

The major forms of metal and liquid speciation for the waters (1-10) at their measured pH are given in Table A.4. If the percent of a complex is less than 0.5%, they are not included.

Aluminum (see Table A.4) is dominated by free and sulfate complex forms; fluoride complexes are of some importance in the low rate lysimeter. Barium is predicted to precipitate in the low rate lysimeter but not in the high rate lysimeter (except for one sample). Because the ICAP results for Ba have an accuracy of within 2 to 3 times at these concentrations, these predictions are viewed as indicating that $\text{BaSO}_4(\text{s})$ may form in the percolating waters of low rate lysimeter but not in those of the high rate. Ca^{2+} , Cd, Co^{3+} , Cu^{2+} , Mg, Mn, Ni, Pb, TiO^{2+} and Zn are dominated by their free forms (Table A.4) but the sulfate complexes represent substantial portions of the total (10-30%). Na and K are essentially uncomplexed. Hydroxide precipitates of Co^{3+} and TiO^{2+} are predicted to occur in several leachate waters from the high rate lysimeter but not the

low rate - this difference is essentially controlled by the higher solution pH in the high rate lysimeter.

Iron chemistry (Table A.4) is dominated by sulfate complexes in the low rate lysimeter and by sulfate and hydroxo complexes in the high rate. $\text{Fe}(\text{OH})_3(\text{s})$ is also predicted to occur in the high rate lysimeter. The RaSO_4^0 complex dominates in the low rate while Ra^{2+} is the more significant species in the high rate lysimeter.

For anions (see Table A.4) the FeCl^{2+} species forms in the low rate but the free form, Cl^- , is dominant in all waters. Fluoride chemistry is controlled equally by Al^{3+} and Fe^{3+} complexes in the low rate but almost exclusively by Al^{3+} in the high rate. This reflects the higher affinity of F for Al^{3+} . Sulfate chemistry is dominated by $\text{Fe}(\text{SO}_4)_x$ complexes in the low rate lysimeter but by the uncomplexed form (SO_4^{2-}) in the high rate.

The speciation calculations for water 4* (Table A.4) show that if sulfate is substantially reduced without changing the metal concentrations (compare water 4 whose pSO_4 is low compared to that of 4* whose pSO_4 is higher), the dominant form of all metals is free except for Fe and Th. For these 2 metals, sulfate complexes remain an important component of the total. The reduction of SO_4 also increases the proportion of Fe tied up with fluoride and chloride because less sulfate is available to compete for Fe.

As inferred in section A.1, the exact redox potential for these waters is unknown. The calculations of Table A.4 assume that all anions and cations are in their fully oxidized state. Speciation calculations for the various waters are given in Table A.5 for $\text{pE} = 13$, 12 and 10 assuming that iron (Fe^{3+} Fe^{2+}) and sulfur (SO_4^{2-} S^{2-}) participate in redox reactions. A redox potential of 13 has a small effect, allowing the formation of up to 5% Fe^{2+} (see Table A.5). A redox potential of 12 increases the portion of Fe^{2+} to about 25% and prevents precipitation of $\text{Fe}(\text{OH})_3(\text{s})$ in the high rate lysimeter water 6. A $\text{pE} = 10$ increases Fe^{2+} to near 80% of the total; this frees substantial SO_4 concentrations to complex with other metals; much less sulfate complexes with Fe^{2+} than with Fe^{3+} . The quantity of metal sulfate complexes increase at the lower pE to become the dominant complex for such metals as aluminum and lead.

More $\text{BaSO}_4(\text{s})$ precipitation is also induced (see Table A.5). Note that water 4* does not fit the sequence of water 3 to 5 because the pSO_4 is lower than the actual concentration measured in the leachate sample on which the chemistry of water 4* is based.

Speciation calculations are given for Water 1A in Table A.6 in which the sulfate and iron concentrations of water 1 have been increased to $\text{pSO}_4 = 0.89$ and pFe to $\text{pFe} = 0.08$). This represents an increase of 5 times for Fe and 10 times for SO_4 . These calculations describe the chemistry expected in interstitial waters and biofilms of the low rate lysimeters where the Fe, H^+ and SO_4 concentrations are higher. It is also expected that the concentrations of other metals would be higher in these local regions, but they are not increased for the calculations to allow examination of the effects of Fe, H^+ and SO_4 upon the biofilm chemistry.

At these elevated concentration for iron and sulfate, sulfate complexes (see Table A.6) of Al, Cu, Mg, Pb, Zn and Ra over the pH range 0.1-1.5; are even more important than in the model water not containing the elevated sulfate concentrations; Ba is dominated by its solid form. However, the ionic strength does not change substantially because most of the increased concentration of Fe and SO_4 goes into $1\pm$ complexes.

These calculations of Table A.6 also permit estimation of the solids which may form in the interstitial waters of the lysimeter biofilms. The main ones suggested are $\text{TiO}(\text{OH})_2(\text{s})$, $\text{BaSO}_4(\text{s})$ and $\text{Fe}(\text{OH})_3(\text{s})$. $\text{PbSO}_4(\text{s})$ is not predicted to precipitate. Jarosite $(\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6(6\text{H}_2\text{O}))$ and silica $(\text{Si}(\text{OH})_4(\text{s}))$ are not evaluated in the speciation calculations. The precipitation of jarosite can be evaluated by calculating its saturation index. The calculated concentrations of free metal and total metal are given in Table A.7 for Fe, K and SO_4 together with the calculated ionic strength of the 10 waters. If precipitation is thermodynamically possible, the saturation index should be greater than 1. The calculations suggest that jarosite should form in the low rate lysimeter and possibly in the high rate lysimeter. The actual nucleation - crystal growth kinetics of jarosite precipitation will be controlled by higher concentrations of Fe, H^+ and SO_4^{2-} in the biofilms about the pyritic particles and by the dilution of these films by higher pH water applied to the lysimeter. Such sequential mechanisms regain further evaluation than can be provided in this work.

The silica concentrations measured in 4 of the leach samples are given in Table A.9. The saturation index is close to 1 for most samples suggesting that precipitation reactions may be occurring in the lysimeters.

Another method for examining Si chemistry is to discern whether all silica possible is in the waters. Orthosilicic acid will originate from proton attached upon quartz, K-feldspar and other alumino-silicates which compose the bulk of the tailings. Concentration ratios of elements in leachate can be used to assess the possible formation of secondary precipitation solids. The element in the denominator may be thought of as a normalizing agent - if the normalizing element is conservative (i.e. does not undergo reprecipitation), changes in the ratios in the leachate compared to that in the parent mineral allows statements about whether the element in the numerator is also acting conservatively or whether it is being reprecipitated.

Concentration ratios of Si/Al, Fe/Al, F/Al, Ca/Al and Mg/Al are presented in Table A.8 for the various leachate waters and for the bulk solids. The Ca/Al ratio in the leachate brackets the ratio observed in the tailings. The variation in the Co/Al data (as measured by the standard deviation) probably reflects residual calcium-sulfates formed in the mill whose resistance to dissolution is caused by the random occurrence, at depth of surface coatings from precipitation reactions. The solids sulfate measurements (see A.4) indicate that sulphate is still present. The Mg/Al ratio is consistently higher (50% to 400%) in the leachate than in the bulk solids; but the solids ratio is much lower than found in typical minerals. The K/Al ratio in leachate from the low rate lysimeters is close to that of the bulk solids; the ratio in leachate from the high rate lysimeter is quite variable but much higher than that of the bulk solids by about 4 times. The leachate ratio of the high rate lysimeter is much closer to that expected from the congruent dissolution of minerals such as K-Feldspar and Biotite than is the ratio from the low-rate lysimeter. It would be useful to measure the actual ratios in the lysimeters solids to ascertain that they are similar to those of the Zahary et. al (1974) data but that has not been done; according the Zahary et. al. data are assumed to be the same for these lysimeters solids.

For silica characterization, then, the first question to decide is whether all the probable forms of K, Mg, Ca and Al and other metals in the tailings are dissolving and leaching stoichiometrically. Na is not a significant fraction; hence it does not warrant

consideration. Other metal concentrations are sufficiently small to not warrant consideration. Because it is possible that mill formed calcium is present, Ca is not a useful tracer (normalizing agent).

Al may be a useful tracer for Si but one must determine whether Al acts conservatively. This can be done by examining various Me/Al ratios. The two ratios, Mg/Al and F/Al, are generally richer in the leachate than in the solids except for the K/Al ratio in the low rate lysimeter where the ratio is smaller than in the solids. The data suggest that the low rate lysimeter may be enriched in magnesium and that the high rate lysimeter is enriched in both magnesium and potassium, relative to aluminum. Enrichment would occur only by retention of aluminum in the solids.

Assuming that modest amounts of aluminum are retained in the low rate lysimeter solids, either some K is also retained in the low rate solids or the K value of Zahary et. al. is somewhat high for these solids. This point awaits further resolution. The K/Mg ratio for the low-rate-leachate is considerably lower than for the tailings solids but the ratio in the leachate from the high-rate-lysometer is similar to that of its solids. It is most probable that K is retained in the low rate lysimeter but not in the high-rate-lysometer. Conclusions (i) that Mg is conservative (i.e. leaches from the lysimeters as it dissolve), (ii) that K is conservative in the high-rate leachate but that some is retained on the low-rate lysimeter solids, and (iii) that Al is retained in both lysimeters is most plausible.

For silica, the Si/Al ratio is near 0.1 before the initiation of the decline of TDS in the low-rate lysimeter. Because it is concluded above that some Al is retained and because the Si/Al ratio is much lower than typical ratios for alumino-silicate minerals, (1:1 to 3:1), silica must be retained in the solids, after dissolution of the alumino-silicate structure by proton attack. This ratio would suggest that more than 90% of the Si from the alumino-silicate is retained. Furthermore, because the silica concentration is approximately the equilibrium concentration for orthosilicic acid-amorphous silica ($\text{SiO}_{2(s)}:K_{sp}=10^{-2.7}$ at 25°C), the data suggest that silica solubility was maintained throughout the leaching history of the low rate lysimeter. That is alumino silicate dissolution leads to the precipitation of the Si as amorphous $\text{SiO}_{2(s)}$ in the biofilms of the low rate lysimeter.

The stoichiometry of the low rate lysimeter ($\text{Si}/\text{Al}=3.8$) at the end of its operation is near that (3:1) of congruent dissolution of typical aluminosilicates (see Table A.8). Because it is hypothesized that some aluminum is retained in the low rate lysimeter, it is probable that some Si is also retained at the time of the end of its operation. This may occur by entrapment of Al^{3+} in the amorphous hydrated $\text{SiO}_{2(s)}$ structure. In the high rate lysimeter, the Si/Al ratio approaches that of the parent solids and the Si is much less than saturated with respect to amorphous $\text{SiO}_{2(s)}$; but it is saturated with respect to quartz ($\text{SiO}_{2(s)}$ $K_{sp}=10^{-3,7}$; $\text{SI} = 4$). The ratio data argue for the dissolution of both an aluminosilicate and of silica while the solubility data argue against dissolution of a quartz mineral. Because the ratio data describe an actual process, it must be concluded that (i) both aluminosilicates and quartz are being attacked by the acid or (ii) only the aluminosilicate minerals are being attacked. Under the latter scenario, secondarily-formed amorphous silicates are dissolving near the end of the leaching history of the high rate lysimeters but saturation with respect to amorphous silica is not maintained because the flushing rate is faster than the dissolution rate. The latter conclusion is more probable.

A.3 Biochemistry of Pyrite Oxidation Reactions from Lysimeters

Oxidation of pyrite is the energy source for the pyrite-oxidizing bacteria T. ferricans. Oxygen is the final electron acceptor for their respiration processes. Ammonia, organic nitrogen and carbon and CO_2 are the main by-products; some phosphorus would also exist in the leachate. The organic nitrogen and carbon originates from remains of the bacterial cells while ammonia results from the release of amino and other NH groups from cells. CO_2 originates from dissolved H_2CO_3^* in the percolating water, air-water interchange in the lysimeter, and bacterial respiration.

The C/N ratio in the lysimeter leachate (Table A.10 which is based upon the TOC/NH ratio on a weight basis) is substantially higher than that expected for typical cells (e.g., 5:1 for $\text{C}_5\text{H}_7\text{O}_2\text{N}$). Only in humic substances do C:N ratios approach 20-30:1. Accordingly, the total N content of the leachate waters is higher than expected; measurements of kjeldahl N are required, but were not carried out herein.

Ratios of $\text{NH}_3\text{N/S}$, $\text{NH}_3\text{N/Fe}$, TOC/S and TOC/Fe are given in Table A.10. The TOC ratios are most relevant in this discussion because of the unknown quantity of organic N in the samples. There is over a magnitude of difference between the ratios in leachate from the low rate and from the high rate lysimeters. This infers that the overall biochemical metabolism of the two sets of lysimeters is significantly different. The samples were stored for 0.8-2.5 years before analysis for TOC and NH_3 . A plot of the rates data over time is not given in this report by inspection shows that there is no trend in the TOC/Fe or TOC/S ratio over time. Accordingly, it is doubtful that the differences are due to metabolic activity in the bottles during storage; because many of the bottles were full (i.e., no air space), aerobic metabolic activity would have ceased shortly after sample collection since bacterial metabolism would be limited by the dissolved oxygen concentration initially present. It is doubtful that a significant amount of S^{2-} would have formed from SO_4 because the TDS measurements made in 1983 and those made by WTC in 1979-81 are essentially the same. In other bottles with head space gas, the large oxygen pool would have allowed for continued metabolism. In some bottles from the low rate lysimeters, microscope examination (see Table A.1) showed that filamentous structures existed whose shape is consistent with that of T. ferrocanis. Accordingly, some bacterial metabolism did occur in the sample bottles; the energy source for this metabolism is probably oxidation of Fe^{2+} which was incompletely oxidized in the low rate lysimeter

It is asserted herein that the TOC/Fe ratio results from metabolic differences in the lysimeters. The same quantity of energy is available from the oxidation of pyrite in both sets of lysimeters, hence the same biomass of bacteria is expected. One can argue for hydraulic differences - a higher hydraulic flushing rate would be more effective in removing constituents from soil moisture and biofilm than a lower flushing rate by physically eroding more of the biofilm. But the TOC/Fe ratio should be the same in the two lysimeters of different flushing rates; the only difference would be that the absolute concentration of both TOC and Fe would be higher in lysimeters with a lower flushing rate. Iron precipitation cannot be argued because its chemistry is dominated by complex formation with SO_4^{2-} in many of these waters and because a similar difference in the TOC/ SO_4 ratio is observed for leachate from the low rate and high rate lysimeters. The differences must be caused by overall metabolic differences between the lysimeters.

The metabolic differences can be ascribed to oxidation of the cellular remains of the pyrite-oxidizers by heterotrophs capable of functioning in water of pH near 1. Their metabolism will convert the TOC of cellular remains of pyrite-oxidizers to CO_2 and more TOC. The data suggests that at least 90% of the TOC formed is lost through this mechanism (compare the ratios of the low rate and high lysimeters).

A similar loss from the biofilm can be invoked for nitrogen. While some errors exist with using the NH_3 data for estimating N, the amount of N in organic form should not change the N concentration by more than 4 times. But the difference in N/Fe ratios between the low and high rate lysimeters is over an order of magnitude (20-40 times). Accordingly a quantity of N similar in magnitude to that of C must be lost from the cellular remains in the low rate lysimeter. Volatilization of ammonia in significant quantities is possible, but ammonia volatilizes as NH_3 , and the concentration of the unionized form is over 8 orders of magnitude below 5 mg/L in these waters. Loss by N_2 formation is another possible mechanism, but it is difficult for denitrifying bacteria to function at low pH. Their presence is possible because the reactions involved for pyrite dissolution (attack on the FeS_2 structure by Fe^{3+} to release Fe^{2+}) provide for low Eh zones. But ammonia oxidation is necessary to provide the NO_3 for denitrification. Nitrification at low pH is strongly inhibited (EPA, 198-).

A calculation can clarify the probable mechanism. Assume that the ammonia concentration in this biofilm is 25 mg/L, the ammonia concentration in the percolating

water leaving the lysimeter is 5 mg/L and that the biofilm is 10 μm thick. The rate of loss by volatilization is equal to the mass transfer coefficient of volatilization times the concentration of ammonia (unionized molecular concentration) divided by the mass of ammonia per unit surface area. For $\text{NH}_3 = 10^{-8} \times (\text{NH}_3 + \text{NH}_4^+)$, the loss rate by volatilization is 0.1%/day. For washout, the loss rate is equal to the concentration in the outflow times the outflow concentration divided by the mass of ammonia present in the films. For the low rate lysimeter, the outflow rate is about 0.1 L/day. The mass present in the films is equal to 25 mg/L times the volume of film water (the surface area of the particles times 10 μm). Assuming the tailings are essentially 90 kg of 70 μm spheres whose density is 2.65 gm/cc, the surface area in one lysimeter is $1.46 \times 10^3 \text{ m}^2$. This gives a loss rate by washout of 0.14%/day. Because volatilization is of the same order of magnitude as the loss rate by washout, volatilization of ammonia is the most probable mechanism for loss of nitrogen from the biofilm in the low rate lysimeter. Its significance will be substantially less in the high rate lysimeter because washout is an order of magnitude higher and because more of the void spaces are more continuously occupied by percolating water.

The data suggest that the yield of cells from pyrite oxidation is at least as large as 170 mM C/m Fe and 50 M C/MS. Assuming that insignificant oxidation of TOC occurs in the high rate lysimeters, these values would be the actual yield. This yield compares with literature values of yield of 0.1 gm TOC per M (or gm) Fe.

A.4 Characterization of Lysimeter Solids

Cores have been taken from the lysimeters (L1, L2, L7, L8) and analyzed for bulk chemical parameters of sulfide, sulfate and carbonate composition, and physical parameters of porosity, moisture content, and bulk density. Occasional samples were analyzed for the radioisotopes of Ra-226, Th-230, Th-232, and Th-228. The appearance of the cores as they were split and sectioned is given in Table A.11; available data for the chemical and physical composition of the tailings is given in Table A.12. The cumulative mass of radionuclides in leachate is compared to the initial mass present in Table A.13. The particle size distribution of the tailings as given in Figure A.13.

A.4.1 Physical and Chemical Characteristics

Of physical parameters (see Table A.12) the bulk density and porosity are quite consistent, being the same for all for lysimeters. The average bulk density is 1.31; the porosity whose average is 0.52, is based upon an assumed density for the solids of 2.75 g/cc. A few density measurements were made to assure that this value for solids density is valid. The moisture content shows a gradation with depths. The moisture content of the 2 high rate lysimeters is somewhat higher than thereof the low rate lysimeters with the exception of the bottom section of L7 (the low rate lysimeter). Because the lysimeters have been shut down for one year before analyses, the moisture contents reflect the result of drainage from the bottom and evaporation throughout the column, starting at the top. The data suggests that at the time of operation, the lysimeters held at least 0.2% moisture by volume. It is probable that a higher moisture content existed during operation and that a higher moisture content existed in the high rate lysimeters than in the low rate lysimeter. The actual content cannot be assessed at present; a close approximation could probably be obtained by restarting subcores and applying water at the original rates.

The importance of the moisture measurements is that it provides for the maintenance of very limited thicknesses of biofilms to the present date. A moisture content of 0.05% corresponds to a biofilm thickness of less than 1 μm in the lysimeter assuming a surface area of $1.5 \times 10^3 \text{ m}^2/\text{lysimeter}$. Hence, the present lysimeters (1 year after cessation of water application) would have a bacterial metabolism which could continue to the present time; it is most probable that the rates of oxidation would have decreased if the

end products in the biofilm inhibit oxidation. Maintenance of a viable but ... community of organisms is possible. Such a community should rapidly respond by recommencing active growth of water application was reinitiated.

The porosity (Table A.12) is larger than that assumed (0.4) for the pore volume calculation and the graphing of radionuclide concentrations versus pore volumes in such figures as Figure 10. These figures could be corrected by calculation of the appropriate factor. But first a correction to the porosity of Table A.12 is required. Some degree of compaction occurred during the coring of the lysimeters. Both L1 and L2 contained 100 cm and 97 cm respectively of tailings but only 85 cm exists in the core tubes. The difference is attributed to compaction. Accordingly the true porosity of the lysimeters is $(0.52 \times 85 \text{ cm}^3/\text{cm}^2 + 13.5 \text{ cm}^3/\text{cm}^2)/98.5 \text{ cm} = 0.59$ and the true bulk density is (0.41) (2.75) or 1.14 at the conclusion of the leaching period. Hence defining the lysimeter pore volume as the flow rate times divided by the void volume, the number of pore volumes on the graphs are high by $(0.59-0.4)/0.59 = 32\%$.

The colouration of the lysimeters correlates quite well with the chemical analyses for sulfide and sulfate. The colour is not affected by carbonates because none were detected. It is probable that the typical levels of carbonates found in the mill discharge (0.02%) are easily and quickly dissolved by proton attack in the tailings during the initial development of acidity reactions from pyrite oxidation. Most of the significant colour trends are expected to be due to pyrite oxidation and precipitation reactions coupled with the natural colour of the quartz solids rather than to gypsum effects.

In the low rate lysimeters, significant pyrite reduction has occurred down to a depth of ca 50-60 cm in L1 and 40 cm in L7 (see Table A.11). No sharp changes in colour are noted in L1; rather it has a uniform buff colour through much of the core with occasional "pyritic" lenses observed below 50 cm and a darker colour observed below 70 cm. For L7, large dark clusters of pyritic particulates are observed at 37 cm showing this to be the redox zone. Below this, increased numbers of pyrite lenses and a grey colour become more prominent. For the high rate lysimeters, L2 and L8 are both significantly leached of pyrite down to 70 cm. Colour wise, the grey pyrite zones start at 76.5 cm in L2 and at 78 on L8. This zone is delimited by an orange $(\text{Fe}(\text{OH})_3(\text{s})-\text{FeSO}_4(\text{s}))$ band, 0.3 cm thick, separating the upper buff colour from the lower grey colour in L2. In fact then, the values for pyrite content in the 70-80 cm of L2 and L8 is concentrated in the bottom 3.5

cm of L2 and 2 cm of L8. This makes the sulfite concentration in Section 8 of L2 similar to that of section 9, but makes the concentration in section 8 of L8 5 times that of section 9. The varying concentrations in section 9 of each lysimeter reflect whether or not care was taken to avoid mixing the silica sand placed in the lysimeters before tailings insertion with the remainder of the tailings of that section.

The pyrite particles are noted to occur in clusters (2-5 mm in diameter) and in lenses. Layering occurs in tailing piles because of the different settling rates of pyrite and quartz particles from the mill FN tank slurry. Accordingly, despite the attempts to homogenize the tailings before placement in the lysimeter, some stratification remained intact. The bottom section data suggest that pyrite concentrations in the lysimeter would have been a minimum of 3% as sulfide by weight when the tailings were placed, assuming no significant movement of pyrite particles from above. The pyrite content was not measured upon initiation of the experiment, but such a value is consistent with observations on other Nordic tailings. Calculation of TDS generated under assumptions of the portion generated as Fe and S would permit a check on this value.

Also of interest is the generally lower concentrations of sulfide throughout the bottom 40cm of L1 compared to the bottom sections of L2 (see Table A.11). This comparison suggests that the lower flushing rate of L1 allows for deeper oxygen penetration and hence more uniform oxidation of pyrite throughout depth. But higher concentrations in L7 (low rate) versus the lower concentrations of L8 complicate this argument. Some guidance is provided by the physical description (Table 4.5.1). There are many areas of a dark orange brown colour in addition to the dark gray pyrite colour. It is possible that surface coatings have developed in L7 on some of the pyrite particles precluding their oxidation. The lower concentration throughout the bottom of L8 compared to that of L2 infers that pyrite oxidation is somewhat more complete in L8 than in L2. This is confirmed by the slightly deeper depth of the oxidizing layer in L8 and the probable mixing of the pyritic layer with the silica sand layer in L8. (see discussion of Ra-226 concentrations below).

The sulfate chemistry of the bottom layer (Table A.12) also complicates the picture. Some residual sulfate is left in all lysimeters where pyrite still exists. This could result from the downward movement of percolating waters whose large sulfate and small calcium concentrations are sufficient to slow gypsum dissolution. But the actual timing

of gypsum dissolator is not correlated with the oxidation of pyrite - gypsum is significantly dissolved in both L1 and L2 relative to L7 and L8. One could argue that complete dissolution would occur when local pyrite oxidation is near complete. The variance in the data does not allow one to confirm such an argument.

The radionuclide data (Table A.12) also permits substantial insight for modelling the geochemical behaviour of acidifying tailings. It has been hypothesized previously (Snodgrass et. al. 1982) that radium is coprecipitated in the leaching pachucas; this coprecipitate in turn is covered by a gypsum precipitate formed in the partial neutralization and final neutralization tanks. Further thorium chemistry is hypothesized to consist of transport through the mill until the final neutralization tank where the raised pH forms a $\text{Th}(\text{OH})_4(\text{s})$ which is emeshed in gypsum precipitate. Then thorium is hypothesized to remain intact on particles in the tailings pile during gypsum dissolution; but when the pH becomes quite acidic, all thorium exposed to acidic pore waters are hypothesized to solubilize and to travel with acidic water. The thorium concentration on solids (see, for example, Table A.12) increase through the mill consistent with this hypothesis. Further the present concentrations (see summary in Table A.13) on the lysimeter solids are an order of magnitude lower in thorium suggesting that thorium formed in the mill has been leached. No significant stratification is observed in the lysimeter data. These data do not absolutely confirm the hypothesis for thorium, but it provides evidence in support of it.

Radium-226 is distributed fairly uniform vertically in L7; the low value in section 9 results from mixing tailings with silica. The more uniform concentrations measured in lower depths of L8 suggest no mixing of the tailings with sand in L8-9. Significant quantities of Ra-226 have been lost from section 1 of L8 (L8-1). Concentrations for lower layers suggest an enrichment immediately below the surface layer and a gradual decline below. This suggests that some radium released from the surface layer is retained at lower depths, either by reversible adsorption or by coprecipitation. Given the water chemistry speciation calculations of (Section A.2), reprecipitation with a barium sulfate solid is probable. Accordingly the mechanism suggested is one in which L8 has reached the stage where pyrite oxidation reaction are sufficiently complete that the sulfate minerals retaining the Ra-226 as a coprecipitate begin to dissolve. Dissolution occurs. But at a lower depth, a higher sulfate environment occurs, causing some reprecipitation.

This scenario is consistent with observations on Ra-226 and TDS in the leachate from L8. A pulse of radium came through the high rate lysimeter during the last year of lysimeter operation; during this time, TDS declined by an order of magnitude. The Ra-226 pattern had a time history characteristic of a chromatographic column. The surface layer of L8 is a candidate source for this pulse; the peak was not maintained continually because of reprecipitation reactions. But under normal conditions, it is expected that the solubility of the parent sulfate mineral containing the Ra-226 would be maintained in the pore water; hence a continual bleed of Ra-226 would be expected rather than the decline observed. There are obviously some local dynamics in the 10-20 cm layer occurring which do not allow dissolution of more of the sulfate mineral. A possible explanation is the high sulfide concentration in Section 1 of L8 (Table A.12). But why it is not oxidized completely before lower zones are oxidized is unknown; an obvious explanation is the formation of surface coatings on pyrite particles which have only recently dissolved. Upon dissolution of the coating, pyrite oxidation in the surface layer then provides sufficient pore water sulfate to prevent further dissolution of the sulfate mineral containing Ra-226 at lower depths.

The mass balance on radionuclides (Table A.13) suggest that little Ra-226 has left the lysimeters to the present time; the mass balance is not closed because initial Ra-226 concentration in the solids at the commencement of leaching were not measured. An order of magnitude higher quantity of radium has left the high rate lysimeter than the low rate lysimeter. Approximately 6-8% of all thorium species have been leached except for Th-228 in the high rate lysimeter which has lost 30%. Because the present Th-228 concentration in the low and high rate lysimeters are essentially the same, it is probable that the larger flux of Th-228 results from a greater isotopic partition of one of Th-228's parents in the high rate lysimeter than in the low rate lysimeter.

Correlations of radionuclide concentrations in the leachate (not given here in) were made with pH and TDS. Of particular note is an inverse correlation between solution pH and thorium activity (Th-228, Th-230 and Th-232). That is with a higher proton concentration, the thorium concentration is higher. These results are interpreted to mean that all thorium left in the lysimeter solids are the original thorium species not mobilized in the mill and that higher proton concentrations are more successful at attacking the residual thorium minerals than are lower proton concentrations.

The particle size distribution of lysimeters L7 and L8 solids (Figure A.13) show no significant differences with depth or between lysimeters. The mean grain size is close to 0.25 mm; the portion of the size distribution between 2 mm and 50 μ m, -95%, is quite atypical of solids examined by Murray and Moffett (1977) who found that 64% was between these 2 size ranges. These tailings may be described as very coarse tailings which have lost all fines of significance. This explains the lower Ra-226 concentration - an average composite mill tailing has 375 pCi/g while coarse tailings characteristically have nearer 165 pCi/g.

APPENDIX B

DESCRIPTION OF LYSIMETER SOLIDS USING SEM-XRE AND MOSSBAUER TECHNIQUES

B.1 SCANNING ELECTRON MICROSCOPE - X-RAY EMISSION (SEM-XRE)

A comprehensive analysis of the lysimeter solids was undertaken. Detailed analysis of samples from the top and bottom section (Sections 1 and 8) have been made. Samples were also obtained from an operating mill (Samples collected complements of A.V. Vivurka) from the leaching pachucas (LP); the partial neutralization (PN) and the final neutralization (FN) tank discharges. Samples of the solids were prepared for analysis by placing dried solids on a carbon stud and coating them with a gold/palladium coating.

Preliminary SEM photographs showed crystalline materials attached to the surface of the quartz grains from the lysimeters. An effort was made to remove these crystals by ultrasonication techniques so that they could be more closely examined in the XRE without interference from the silica matrix of the quartz grams. Several samples were placed in 130-octane tone and ultrasonicated for 30 minutes; the solids were allowed to settle and the suspended particles and iso-octane were decanted. The solids from the LP and Sections 1, 4, 8 of lysimeter L8 were ultra-sonicated. Particles from the decant were removed with a pasteur pipette and placed upon the carbon stud for analysis; the stud was left uncoated.

In this Appendix, emphasis is placed upon the results from the mill solids to give a qualitative indication of the nature and composition of the solids before their disposal. Then selected SEM electronmicrographs from lysimeter L8 are described.

Fig. B.1 - B.2 show solids from the LP; the host solids are coated, to varying degrees of coverage, with particles which appear to be precipitation - products formed in the leaching pachuras. The XRE (of Fig. B.1) shows that the whole field is dominated by Si with significant amounts of Al, K, Fe and Ca present; significant amounts of S are not present. Fig B.2 has small dendritic solids covering the parent silica particle and the 10 um plate. The whole field is dominated by Si with Al and K present. Analysis of the two plates (2-10 um) in the centre of the picture have the same composition - they are enriched in Al and K relative to Si compared to the whole field. It is probable that the

actual Si content of the small plates is much smaller because the depth of field of the SEM beam (about 1 μ m) picks up Si from the larger parent solid. These plates are the probable mineral which undergo proton attack in the lysimeters (L1-L8). Analysis of other sectors of the electron micrograph (not given) show similar behaviour with Al, Si, KC, Fe, Cu, Ca and S being present in significant amounts but in varying ratios. This suggests that perfect crystals are not formed but rather crystals are formed in the L.P. which have quite a variable composition.

Solids from the PN appear to be covered to a higher degree of surface coverage than those of the LP (see Fig. B.3); this may result from gypsum precipitation in the LP. The surface coatings are quite fibrous with many small void spaces. The whole field of Fig. B is dominated by Si, but significant amounts of Al, K, Ca, Fe and S are present suggesting aluminosilicates, gypsum and pyrite. The whole field of Fig. B.4 is dominated by Si with lesser quantities of Al, S, K, and Ca. Fe is not present in significant quantities. The center of the large particle (triangle shape) is dominated by Al, Si and K while the rod to the lower left is enriched in Ca and S relative to Al and Si; no K of significance is present. The structure is consistent with gypsum overgrowing (overlying) an Al Si structure. The lack of K may be due to the detection limit of the XRE given the large concentration of Si.

The final tailings qualitatively show a similar density of cover as the PN. Of note are certain distinct structures. The whole frame of Fig. B.5 has Al, Si, K, Ca, Fe, and S present in significant amounts. The 20 μ m particle in the middle is a pyrite particle with some Al, Si and Ca of significance. The whole field of Fig. B.6 is dominated by Si and CaS; Al and K are also present in large quantities with minor amounts of Fe. The rod in the middle is enriched in Ca and S but contains significant quantities of Al, Si and K. The morphology of the rod is consistent with ettringite (calcium sulfate aluminate hydrate), one of the solids important in chemical reactions of concrete. Hence whether pure gypsum or ettringite type particles form in the mill is a question which will require further work.

The degree of covering of parent solids by precipitates in lysimeter 8 is much less than those of the final neutralization tank. (contrast Fig. B.7 to B.3). The quantity of Ca and S is routinely much less or non-existent. The whole frame of B.7 from the top section of the high rate lysimeter L8 is dominated by Si and Fe; no S of significance is noted. This

suggests silica and iron hydroxides as the dominant forms. This is consistent with the physical description of the core involving a deep orange colour and a rose coloured band that 3 cm i.e., an $\text{Fe}(\text{OH})_{3(s)}$ covering silica particles. Figure B.8 centres upon a flaky structure cemented to the edge of a host quartz particle. The whole frame is dominated by Si; some Al, K and Fe is present. The relative enrichment of the flaky structure by Al and K suggests that it is a reformed Al-Si-K structure.

The surface of the bottom section (70-80 cm) is more densely covered with rods, polygons and dendrite than the top section. Fig. A.9 contains Al, Si, and K with small amounts of Fe and S; the rod in the middle qualitatively contains approximately the same portions of Al-Si-K as the whole field but without significant quantities of Fe and S. This section was described as being the section in which the pale yellow from above was replaced by a dark grey pyrite colour (see A.4). The Fe is probably pyrite while the rod may be a mill-formed or a reformed alumino-silicate. The composition of Figure B.10 (Section 8, L8) is curious. The field has significant quantities of Mo and Ca present. The small (10 μm) particle in the middle of the large particle is dominated by Mo and "Ar" and slightly enriched in Cu relative to the whole field. No Al, Si or Ca is present. Ar is not probable; hence the peak from a nearby metal on the spectrum is being misinterpreted by the XRE. This picture provides an illustration of some of the care required with use of the SEM-XRE technology.

The last 4 electronmicrographs present a few results from the ultrasonicated experiments. A curious flaky-shell type structure was isolated from the leaching pachucas (Fig B.11). The structure is mainly Si and S with lesser amounts of Al, K, Ca and Fe. Fig. B.12 was isolated from the surface section of the high rate lysimeter. The amorphous appearing particle at the middle of the picture is mainly Al and S. Fig. B.13 shows the distinct morphology of pyrite crystals from section 5 of L8. There are large amounts of Fe, Si, K and Ti in the center of the field. Fig. B.14 (70-80 cm depth of L8) shows a wide spectrum of particles removed by ultrasonic vibration. Si dominates the picture with significant amounts of Al, K, Fe and S present. Other fields of view show that fields with many pyrite crystals are dominated by Si with lesser amounts of FeS and even smaller amounts of Al and K.

That such fields may be dominated by Si shows that further work with ultrasonic techniques are required to examine the form of the $\text{SiO}_{2(s)}$ and to isolate it to allow

identification of other spectra. It may originate as part of the original ore, broken down to these sizes in the mill. It may result from acid attack on silica in the tailings, leading to cleavage sites developing. This is possible because similar dominance by Si was not observed in the ultrasonicated mill samples. The amorphous appearing forms may represent reformed silica or aluminosilicates as suggested by the analyses of metal ratios in the lysimeter leachate. During reprecipitation, migrating radioisotopes may be coprecipitated in significant quantities. Hence these structures cannot be neglected.

To examine other structures, removal of the SiO_2 structures might be accomplished by differential centrifugation or timed gravity separation. Use of SEM-XRE techniques hence require more work and creative sample preparation techniques to attain its potential.

Discussion

The use of the SEM-XRE in this project shows a few points of interest and a few areas which require more work to allow it to fulfil its potential capabilities. This analysis provides evidence for the formation of precipitates in the leaching pachucos, the formation of dense coatings in the PN and FN tanks and a dramatic decrease in the surface area of host solids covered by these coatings in the leached tailings samples. The denser degrees of coverage by coatings on host solids at the bottom lysimeter 8 compared to its top section is correlated with (i) the leaching behaviour, (ii) the occurrence of probable iron hydroxide bands, and the complete oxidation of pyrite in the surface layers and (iii) chemical measurements of sulfides and sulfates. The coatings are not uniformly thick, but rather quite porous. The coatings provide a large surface area for adsorption but cause difficulties for selecting "model" structures to used for mathematical modelling of the geochemical evolution of tailings piles.

The following points arise from this work and our discussions concerning use of SEM-XRE for future tailings work.

1. The work at present has shown SEM-XRE to be capable of rapidly resolving different structures in a semi quantitative manner. Standards would be required to allow quantitative determination of masses of elements present in the field of view.

2. A set of standard structures are required for incorporation into the SEM-XRE library. The structures would include mineral name and quantities of different elements in each mineral. Sample analysis would then be followed by the SEM-XRE microprocessor searching the library and almost instantaneously giving statements about the most probable minerals present and their respective masses. A library particularly tailored to uranium ores, mill-formed precipitates and secondary precipitates formed during weathering reactions would be particularly valuable. Development of such a library is quite analogous to the libraries of morphology and Xray spectra developed for XRD instrumentation.
3. Identification of Fe minerals, particularly secondary minerals formed by weathering reactions (e.g. jarosite) has some difficulties because of the occurrence of Fe and S as pyrite and $\text{Fe}(\text{SO}_4)_x$ in jarosites. Techniques for separating pyrite from the tailings would be useful for mineral identification. Similar developments would be useful for use of Mossbauer techniques (see below).
4. This work has identified the possible existence of an ettringite mineral. Such minerals are important in cement reactions. They are described as a calcium sulfate aluminate hydrate. The chemical concentration of Ca, SO_4 , and Al in mill-waters in the PN and FN tanks in the mill and in the lysimeter pore waters provide for its formation. If present in significant quantities, dissolution kinetics for this precipitate will be required for modelling the geochemical evolution of tailings piles. A useful starting point would be more work to identify its existence and an assessment of the differences between gypsum and ettringite formation and dissolution kinetics.
5. The chemical leachate analysis (section A.2) suggests that secondary aluminosilicates are forming on the tailings due to dissolution of primary minerals and due to solubility controls on orthosilicic acid in percolating waters. The opaque structures observed in lysimeter 8 are possible candidates for this amorphous silica. Because such $\text{SiO}_{2(s)}$ is X-ray amorphous, SEM-XRE provides a technique for their identification. Such structures are candidates for entrapping dissolving radioisotopes by coprecipitation reactions. Analysis of these structures, upon separation from the parent particles, by SEM-XRE, chemical methods, chemical

speciation calculations and for radioisotopes would permit some conclusions concerning their ability to entrap migrating radionuclides.

6. The Al, Si, K ratios vary from sample to sample and within the same solids sample. Different nucleation crystallization reactions are probable because of local concentration differences. Whether the nucleation and crystal growth of these particles is controlled by transport of cations from solution or more as a corrosion reaction at the alumino-silicate surface awaits further work.
7. There is a resolution for identifying elements in precipitates on the parent quartz solids because the quartz solids elominate the spectra. The pointer on the SEM provides an advantage by allowing one to isolate upon the centre of one particular particle (e.g., a rod) and to ask for its elemental composition. Its elemental composition and morphology allow rapid mineral identification. But the depth of field used by the electron beam (e.g. 1/um) often picks up some of the Si from the host solid. Further development of ultrasonic techniques and separation of the precipitates by centrifugation is one possible method for removing the masking effect of the $\text{SO}_2(\text{s})$.
8. A gold-palladium coating on the tailings placed upon the carbon stub is not required to obtain XRE spectra; however the long time required to take a photograph on the SEM (near 100 sec) produces a blurry picture because of the charging effects and associated motion of small particles. Use of a videotape represents one answer to this problem due to its ability to obtain a picture of a changing electron micrograph.

B.2 SECONDARY SEM-XRE ANALYSIS

It was observed that several waters used for the washing of lysimeter solids for gypsum analysis developed a light orange to dark orange colouration within a few hours after the washing. The colour appeared to be an orange fluffy precipitate formed in a previously clear, solids-free water obtained from washing the solids on a filter. These colour precipitates were filtered off for further analysis. The colour of the filter paper is noted in Table B.1. The nomenclature used is as follows: L1-2-8 denotes lysimeter 1, the second core, section 8 (70-80 cm). Wash waters from lysimeter 2 (high rate) were

generally clear although some precipitates developed in the wash waters from sections near the bottom of the lysimeters. Lysimeter 8 (high rate) appeared to have similar behaviour, but more precipitate development was observed in L8. Large amounts of precipitates formed in wash waters from all depths of L1 and L7 (the two low rate lysimeters) except for the surface sections. Some precipitates formed in the mill washings.

The filtered precipitate from L1-2-3, L7-1-8 and L8-1-8 were analyzed by SEM-XRE. The precipitate from the middle of one low rate lysimeter (L1-2-3) was dominated by an Fe S solid; small amounts of Al and Cu were also present. Because the sample should be oxic, the Fe S solid should be an iron sulfate; the form could be $\text{CuFe}_x(\text{SO}_4)_y$; $\text{Al}(\text{OH})_3$ a form typical of jarosite. Debate exists over whether on a basic metal sulfate of aluminum actually forms by precipitation; the evidence of DeHek et. al. (1978) argues against it although substitution of Al into the structure of FeSO_4 is possible.

A search of the filter paper from the bottom of the low rate lysimeter (L7-1-8) on the SEM/XRE shows viable chemical composition. One spot had Zn as the dominant element with some Fe, Ca and Al and a little S present; other spots were dominated by Al, Si, K and Fe with no S. Such behaviour can be explained as an alumino-silicate, precipitation of quartz entrapping Al and iron sulfate or iron hydroxide. The heavy orange colour is typical of $\text{Fe}(\text{OH})_{3(s)}$.

The third filter paper (L8-1-8) from the high rate lysimeter is dominated by Si and Fe with a small quantity of Al. K is present in one location; Ti is strongly present in another location. No S is present. Formation of amorphous silica and iron hydroxide appear to dominate. The presence of Ti as $\text{TiO}(\text{OH})_{2(s)}$ is most probable, particularly given the predictions of its precipitation in the speciation calculations of section 4.4.2. It is possible that Al that K are incorporated into an amorphous $\text{SiO}_{2(s)}$. It is improbable that $\text{Al}(\text{OH})_{3(s)}$ would be significant due to the low pH.

These phenomena provide some evidence that the kinetics of precipitation of iron sulfate as well as iron hydroxide are fairly rapid. The rapid kinetics for iron sulfate and their formation in these solutions are possible because of the low pH - the pH of the waters of L1-2-3 was 3.1 while those of L7-1-8 was 2.9 and those of L8-1-8 was 2.7. But $\text{Fe}(\text{OH})_3$ is more stable than $\text{Fe}(\text{SO}_4)_x$ at pH's 2 (Brown, 1971). Hence the formation of the

$\text{Fe}(\text{SO}_4)_x$ on the L1-2-3 filter paper awaits explanation. Assuming that some of the iron washed from the solids is in a +2 oxidation state (i.e., Fe^{2+}), these phenomena suggest that iron oxidizing bacteria may still be active in the tailings, 1 year after reasation of operation of the lysimeters. Another possible explanation is that the bacteria created a biofilm containing large concentrations of Fe^{2+} after ceasation of lysimeter operations that the bacteria became sesile, and that the oxidation kinetics of Fe^{2+} are sufficiently slow at pH 1 that a large pool of Fe^{2+} still remains.

B.3 MOSSBAUER SPECTRA OF URANIUM TAILINGS SAMPLES (University of Western Ontario)

Mossbauer spectra were obtained from six L8-1-8, L8-1-1, L7-1-1, L7-1-8, L7-1-10 and "Leaching Pachaca Discharge". L8-1-1, L8-1-8, L7-1-1, and L7-1-8 are respectively the top (0-10 cm) and eighth (70-80 cm) sections from Lysimeter 8 (L8); the high rate lysimeter) and 7 (L7; the low rate lysimeter) L7-1-10 is a section of silica sand from the bottom of lysimeter 7 (section 9; depth 84 cm) containing a yellowish colonization and hypothesized to be a redox boundary where jarosite, iron hydroxide or similar precrysalate could form. All samples contained sufficient iron yield satisfactory spectra although samples L7-1-1 and L7-1-10 required large counting times and spectra were only run for a sufficient time to establish they were consistent with the other spectra.

The spectra obtained (figures A15-A17) were essentially identical, with a well resolved ferric doublet and narrow line widths indicating a unique iron containing environment (within instrumental resolution). Four of the spectra were computer fitted with acceptable statistics using a conventional X^2 minimisation program assuming Lorentzian peak shapes. The results of these computer fits are shown in Table B.2.

The parameters shown for Quadrupole splittings and Isomer shifts are consistent with those of pyrite (FeS_2): IS - 0.31 mms^{-1} , QS = 0.61 mms^{-1} . The narrow line widths observed (0.3 mms^{-1}), make it unlikely that a second iron containing species is making any significant contribution to the spectrum. A possible exception is spectrum L7-1-10 where there is evidence of a second ferric resonance, possibly jarosite $\text{MFe}_3(\text{OH})_6(\text{SO}_4)_2$ M- Na^+ , K^+ etc. (IS - 0.43 mms^{-1} , QS = 1.2 mms^{-1}). However, the low levels of iron in this sample make it impossible to resolve such a contribution from the instrumental

sinusoidal baseline. In the well resolved spectra (Leaching Discharge, L8-1-1, L8-1-8, L7-1-8), a significant jarosite contribution ($> 5\%$) would cause visible shoulders, particularly on the high velocity peak. Although in all spectra the higher velocity peak is the larger of the two, the difference in all but spectrum L7-1-10 is within allowable statistics.

We conclude that pyrite is the dominant iron containing species in all the samples examined with a possible contribution from a second ferric iron species in sample L7-1. This could be jarosite. However, the low total iron level in this sample makes it impossible to resolve a second resonance.

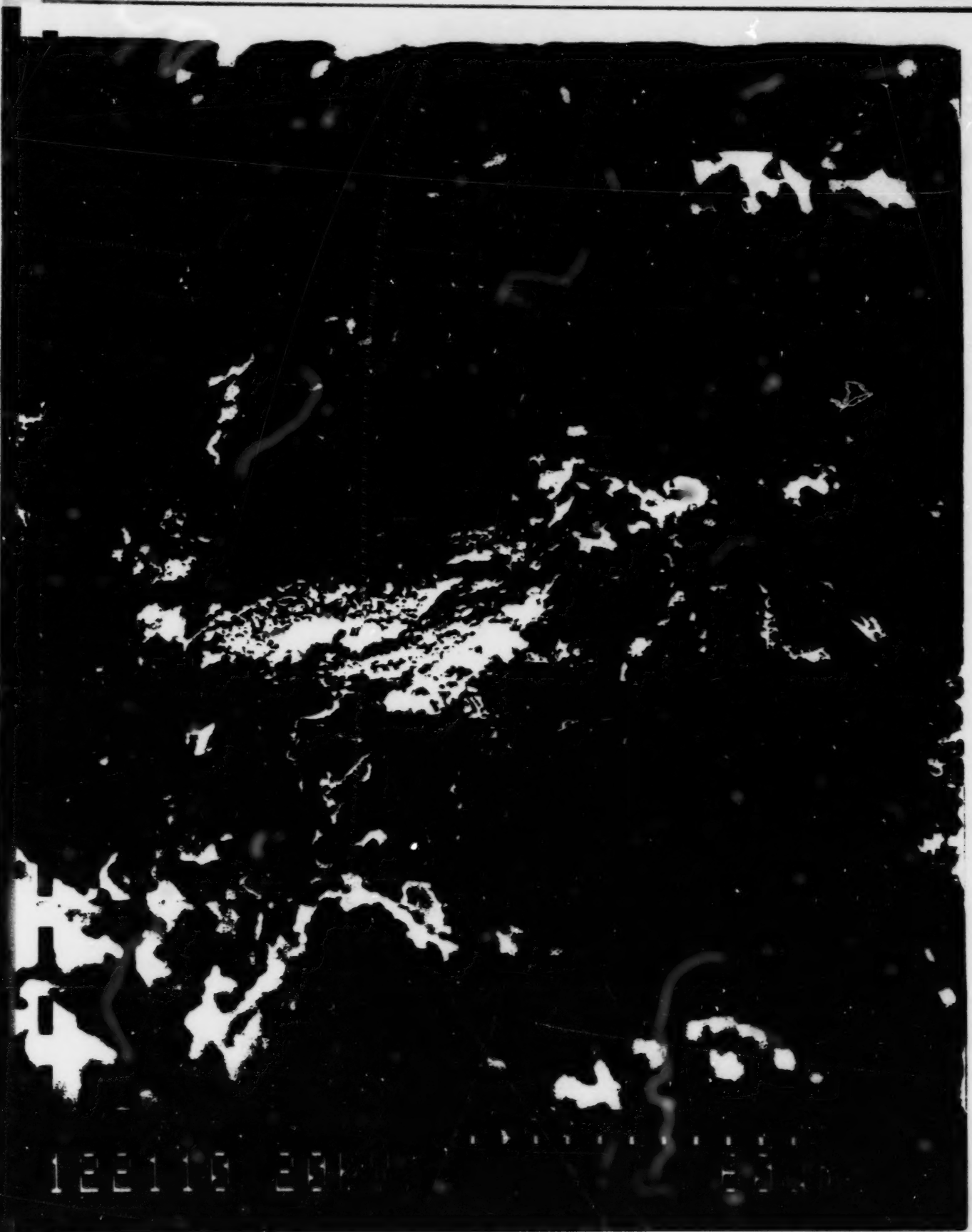
ELS
Leadate Discharge

Whole Frame

Al	150
Si	2283
K	173
Fe	91
Cu	206

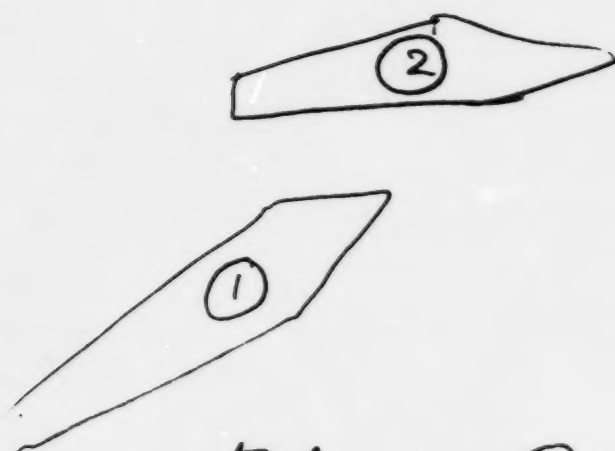
Fig B.1 (122110)

EL
A.



122110 2000

EL 3
Leadate
Discharge



	Whole	①	②
Al	77	393	393
Si	1671	1455	1455
S	—	—	—
K	122	278	278
Ca	—	—	—
Ti	—	—	—
Fe	—	—	—

Fig B.2 (12 21 09)



122109 26

Part. Newt Disc
E Lake Tautog

Whole Frame

Al	201
Si	1622
S	191
K	229
Ca	274
Fe	109

Fig B.3 (12 21 07)



122107 20KV

3000μm

Part New USCA
E Lake Tailings ①

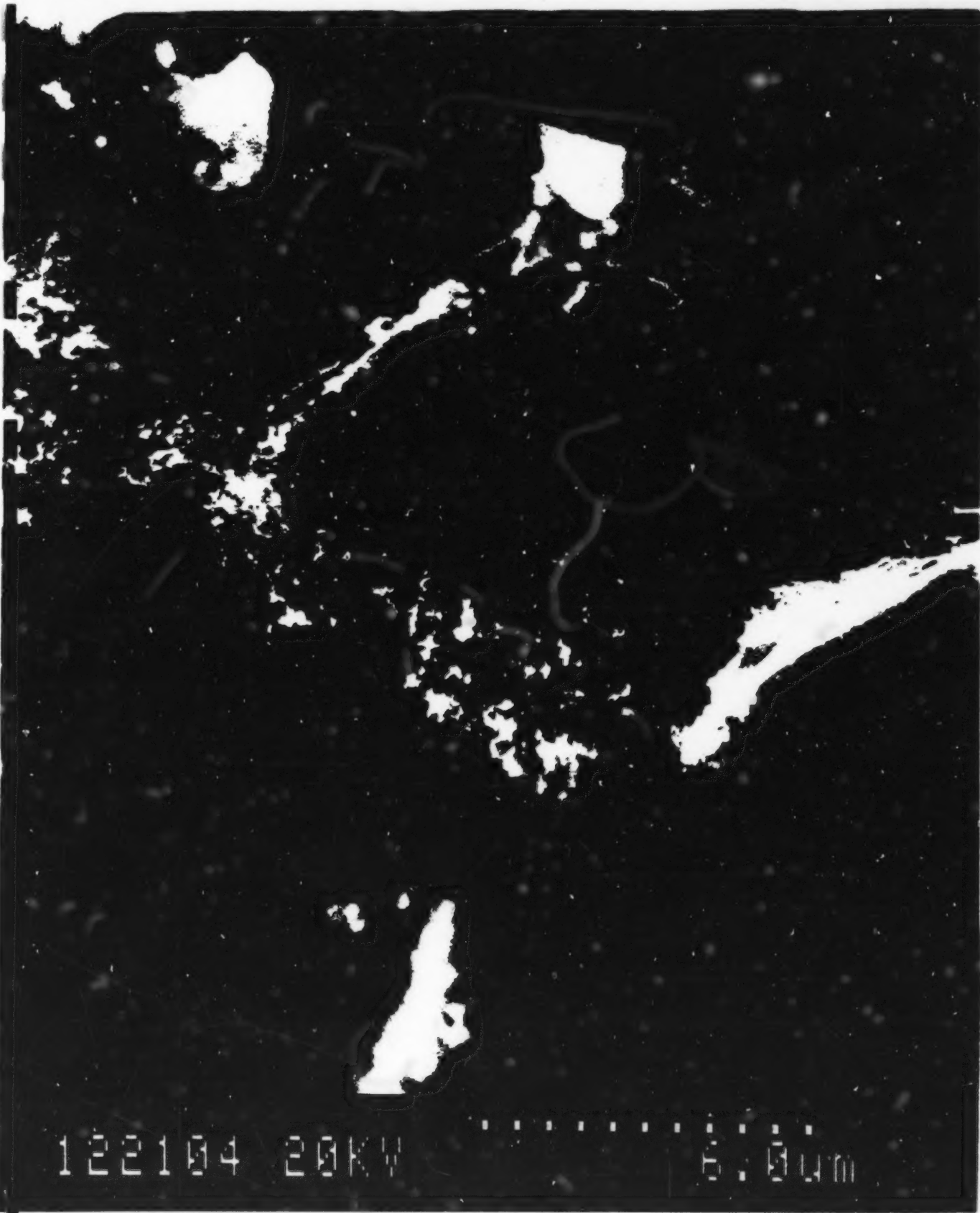
	Whole	①	②
Al	199	578	54
Si	1144	1209	898
S	98	—	350
K	245	381	—
Ca	114	—	455
Ti	—	—	—
Fe	—	—	—

①

②

12 21 04

Fig B-H



122104 20KV

6.0um

Elliot Lake
Final Tailings.

	Whole Frame	Large xtal Course Field
Al	153	103
Si	988	302
S	580	3962
K	173	—
Ca	427	156
Ti	—	—
Fe	203	1908

↑↑
Pyrite or
Tarrosite

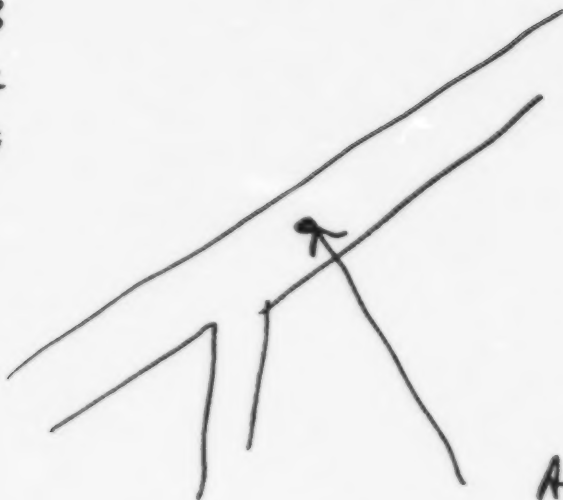
Fig B.5 (12 19 09)



Ellicott Lake
Fruital Tailings

Whole Frame

Al 779
Si 4291
S 1174
il 813
Ca 1114
Fe 140



Al 340
Si 1686
S 1369
K 323
Ca 1367
Fe 86

Morphology consistent with Ettringite
(Calcium Sulfo Aluminate Hydrate)



Fig B 6 (12 09 02)

L 8-1

Same ϕ as 12-21-18 & 19

Area of 12-21-19

Whole Frame

Si 375

Fe 97

Fg B.7 (12-21-20)



122120 20KV

Luminous x100 edge
of sand grain

L 8-1



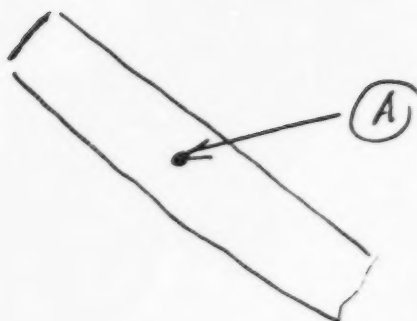
	A	Whole
Al	149	51
Si	753	2565
K	152	77
Fe	141	167

Fig B.8 (12-21-16)

152116 20NW 25.5m

Surface of Sand Grain

LE/S



	(A)	Whole Frame
Al	206	402
Si	1527	2628
K	153	603
S	—	136
Fe	—	126

Fig B.9, (12 21 12)



EL Tals

8/1/1



	Where	A
Al	138	~~135~~
Si	485	—
Mo	352	1991
Ar	—	4361
Ca	658	—
Fe	182	195
Cu	178	222

Fig B.10 (01 16 07)





032004

Fig B.11

171



332005 20

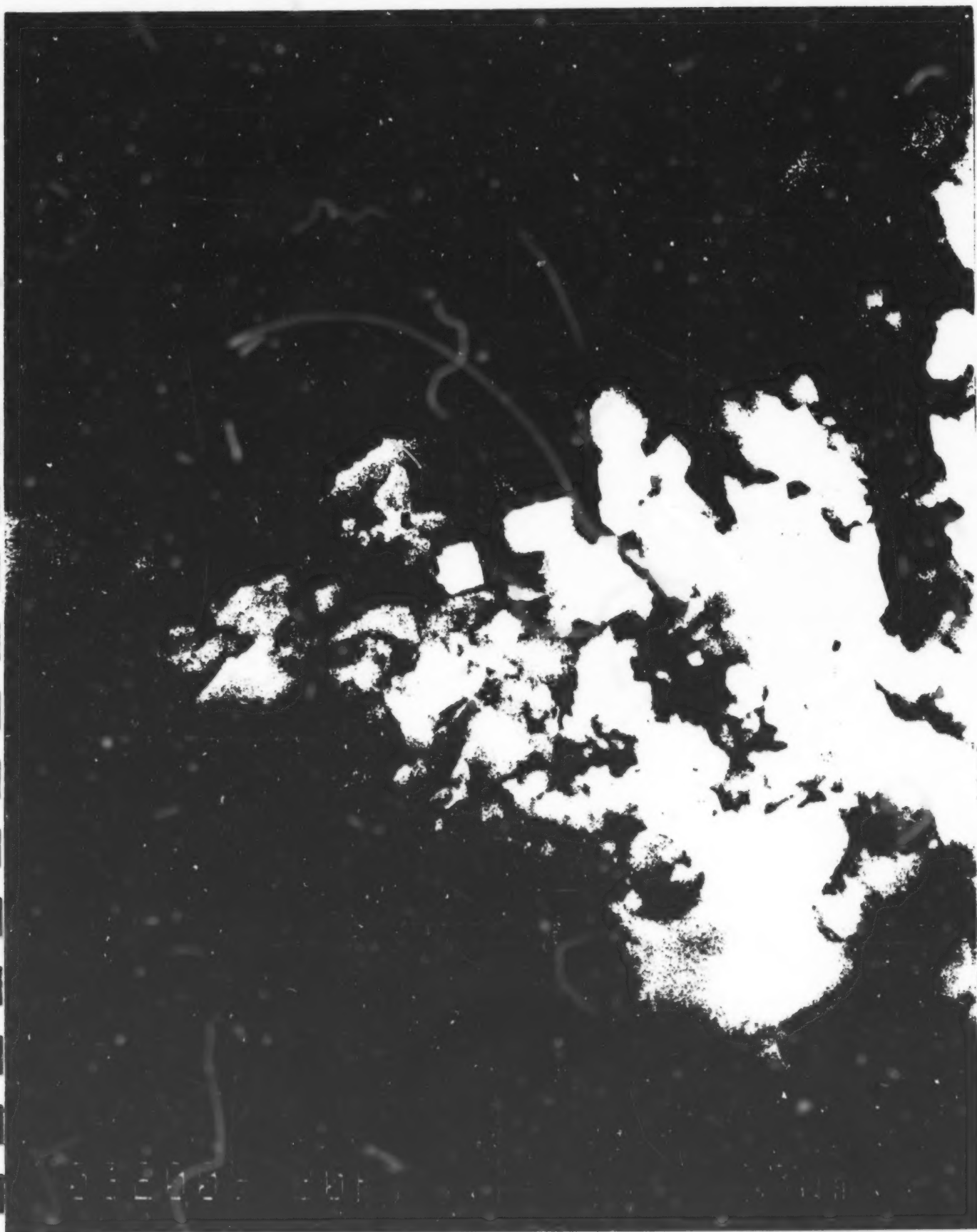
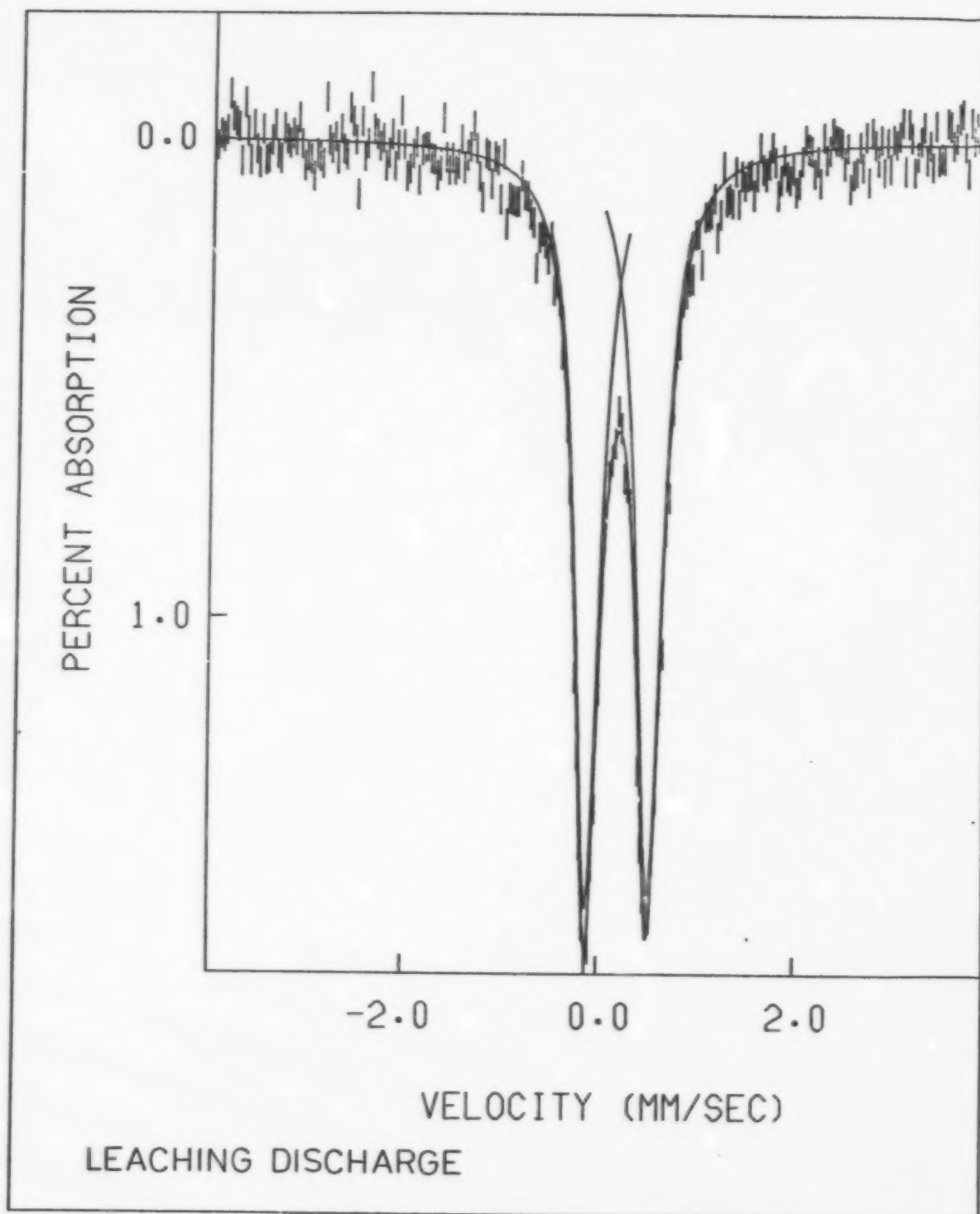


Fig B.13 179



Fig B.14



F. B. 15

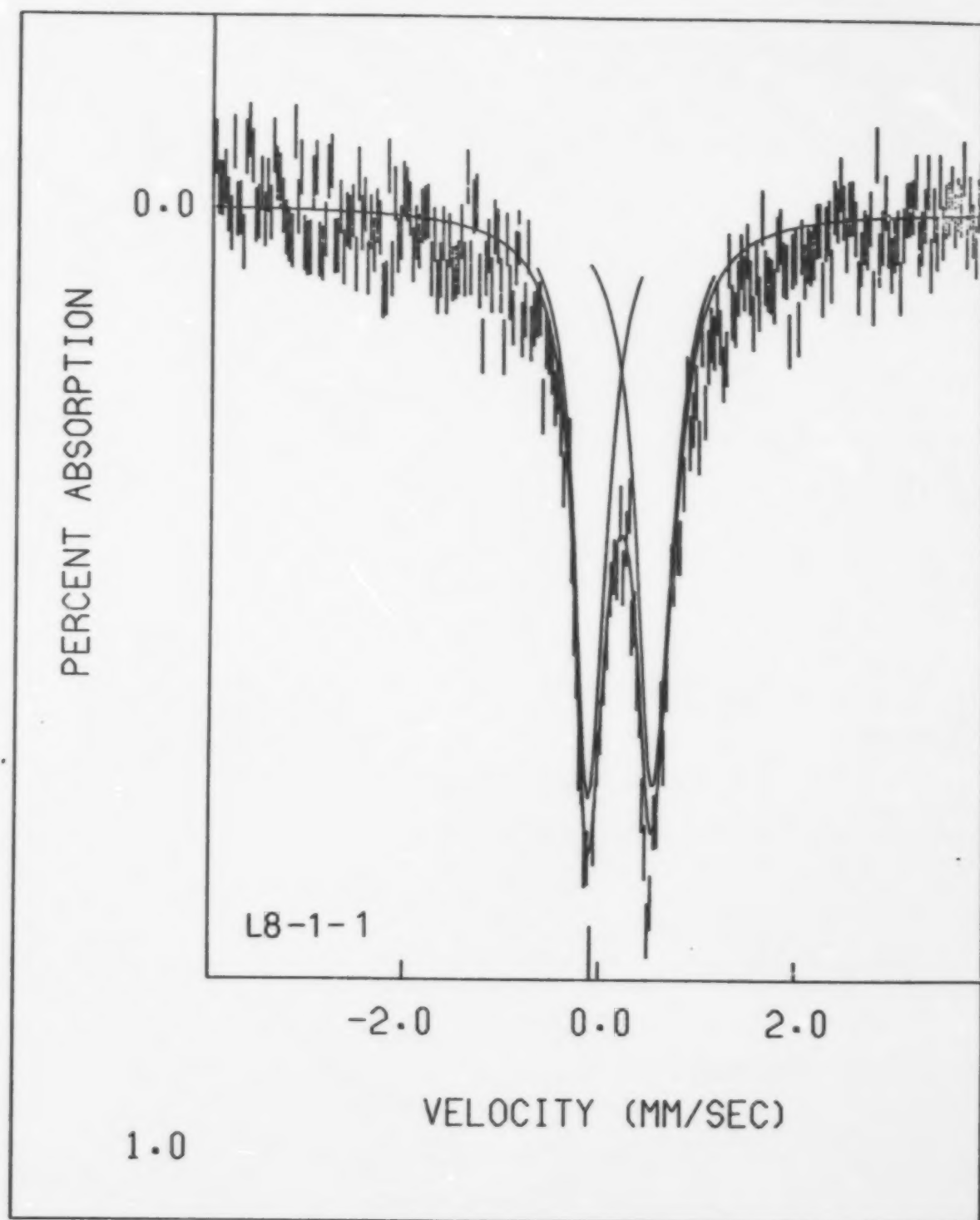
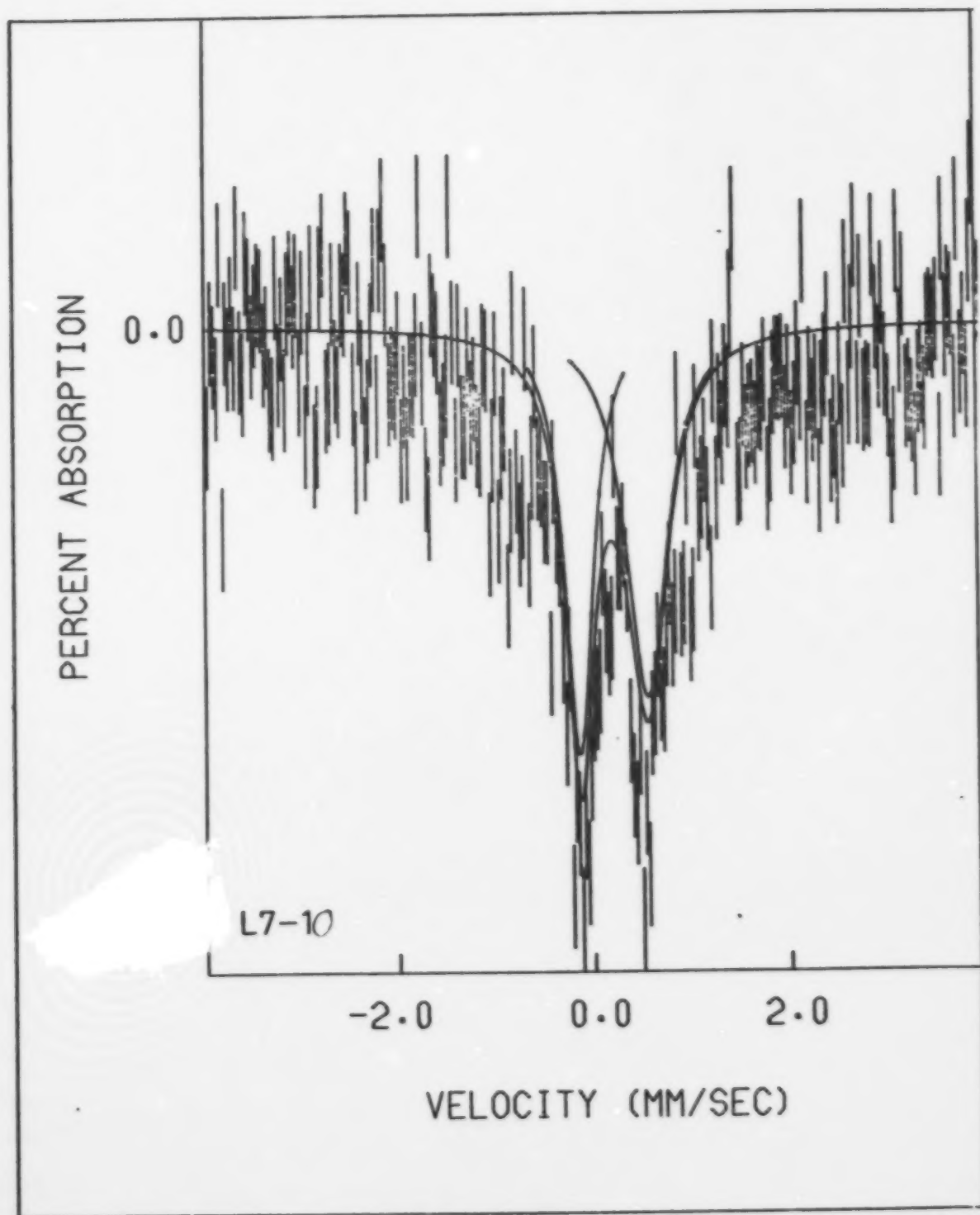


Fig B. 17



F. B. 18